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The crystal and molecular structures of the pentitol penta-acetates

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ABSTRACT

The crystal structures of the 1,2,3,4,5-penta-acetates of ribitol, xylitol, and D- and DL-arabinitol have been determined. A modification (mp 50°, space group $P\bar{1}$) of xylitol penta-acetate was investigated, which is not that (mp 65°, space group $P2_1/c$) usually encountered.

INTRODUCTION

The crystal structures of all of the hexitol hexa-acetates (racemates included) have been reported[1–3] with the exception of that of D-altritol hexa-acetate which resisted crystallisation till now. These investigations supported evidence[4,5] that the steric influence of 1,3-parallel interactions of C and/or O atoms (designated as C//O and O//O, respectively) in acyclic carbohydrates has been overestimated[6].

We now report on the solid-state conformations of the pentitol penta-acetates, knowing that acetylated oxygens could be less sterically demanding than hydroxyl groups[7].

RESULTS AND DISCUSSION

In the pentitol series, three diastereomers are possible, two of which (ribitol and xylitol) are *meso* compounds, whereas arabinitol is asymmetric chiral. Therefore, excluding polymorphs, four solid-state structures have to be considered for the

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TABLE I

Crystallographic data for **1**, **2** (modification with a low melting point), D-**3**, and DL-**3** [a]

Data	**1**	**2**	D-**3**	DL-**3**
Formula	$C_{15}H_{22}O_{10}$	$C_{15}H_{22}O_{10}$	$C_{15}H_{22}O_{10}$	$C_{15}H_{22}O_{10}$
Mol wt	362.33	362.33	362,33	362.33
Mp (degrees)	51	49–51	75	95–96
Crystal dimensions (mm)	0.2×0.1×0.1	0.4×0.4×0.3	0.2×0.3×0.4	0.3×0.3×0.4
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/a$
Cell parameter (pm, degrees)				
a	1255.6(1)	875.8(1)	865.1(1)	871.6(3)
b	1824.2(1)	1053.9(1)	1212.4(2)	1223.6(4)
c	1679.5(2)	1133.9(2)	3570.6(6)	1784.4(6)
α	(90)	67.00(1)	(90)	(90)
β	101.84(1)	80.20(1)	(90)	93.40(3)
γ	(90)	69.70(1)	(90)	(90)
Volume V (pm × 10^6)	3765.0(6)	902.8(2)	3745(1)	1899.7(11)
Z	8	2	8	4
$F(000)$	1536	384	1536	768
Calculated density D_x (g × cm^{-3})	1.278	1.333	1.285	1.267
λ, $K\alpha_1$ (pm)	154.051(Cu)	70.9261(Mo)	154.051(Cu)	70.9261(Mo)
μ (cm^{-1})	8.9	1.1	9.0	1.0
$2\theta_{max}$ (degrees)	130	50	153	45
Reflections (symmetry independent)	4934	2975	4094	2124
Reflections with $F_0 > x\sigma(F_0)$	2270 ($x = 6$)	2370 ($x = 4$)	3264 ($x = 3$)	1148 ($x = 5$)
Number of refined parameters	463	315	627	294
Ratio of valued reflections to parameters	4.9	7.5	5.2	3.9
Final residual factors				
R	0.085	0.062	0.075	0.093
R_w	0.078	0.060	0.077	0.072
Diffractometer	Enraf–Nonius CAD4	Syntex P21	Enraf–Nonius CAD4	Syntex P21

[a] Standard deviations in parentheses.

pentitol penta-acetates, namely, two *meso* compounds [1,2,3,4,5-penta-*O*-acetylribitol (**1**) and 1,2,3,4,5-penta-*O*-acetylxylitol (**2**)], one enantiomer [1,2,3,4,5-penta-*O*-acetyl-D-arabinitol (D-**3**)], and one racemate [1,2,3,4,5-penta-*O*-acetyl-DL-arabinitol (DL-**3**)].

Suitable crystals for X-ray determinations were obtained from solutions in ethanol or ether. The structures were determined in the usual way by direct methods using the programs SHELXS90[8] to solve the phase problem and SHELX76[9] (blocked matrix) for refinement. Hydrogens were introduced at theoretical positions. 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 lengths and angles were observed. The crystal structures are represented as SCHAKAL88-drawings[10] (Figs. 1–5) which also show the atom numbering.

meso-*Pentitol penta-acetates.*—1,2,3,4,5-Penta-*O*-acetylribitol (**1**) and 1,2,3,4,5-penta-*O*-acetylxylitol (**2**) have long been known as crystalline compounds[11–13]. Whereas **1** had mp 51°, as reported[11], we encountered a modification of **2**, mp 49–51° (Table I) (the reported[12,13] mp is 62–65°).

Fig. 1 shows the two independent molecules of **1** as found in the crystal. In order to avoid an unfavourable 1,3-parallel O-2,4 interaction, the central carbon chains are bent into a sickle conformation with the result that individual molecules become chiral. Thus, molecule I has the pseudo-D and molecule II has the pseudo-L configuration and each forms, with symmetry-related molecules, a pseudo-racemate in the crystal. This situation is also observed in ribitol[14]. Also, in **1** and ribitol[14], O-1,5 are *gauche* to their neighbours. This situation is observed generally in alditol acetates[1–3] and often in free alditols, and can be explained by the general "gauche effect"[15].

Xylitol penta-acetate (**2**) usually occurs[12,13] in a modification with mp ~ 62°. Park et al.[1] have reported the structure of this morph (mp 65°, space group $P2_1/c$) shown in Fig. 2. In violation of the "Hassel–Ottar" effect[6], the carbon chain is planar zigzag, and a 1,3-parallel O-2,4 interaction is tolerated. Furthermore, another such "forbidden" O//O interaction (O-3,5) is tolerated. This situation resembles that found in D- and DL-glucitol hexa-acetates[1–3].

In our laboratory, **2** crystallised in a modification (mp 49–51°, space group $P\bar{1}$) not encountered hitherto. As in crystalline xylitol[16], individual molecules adopt a sickle conformation (Fig. 3), avoid O-2//O-4 interactions, and are chiral. In contrast to the parent compound, which forms single crystals of molecules of the same chirality, and as such is found as a pseudo-conglomerate[16], both morphs of **2** are pseudo-racemates[17].

On the basis of the lower melting point and density D_x, the above modification of **2** should be metastable at room temperature despite the fact that the conformations of individual molecules are in accord with the "Hassel–Ottar" rule[6].

Dissymmetric pentitol penta-acetates.—1,2,3,4,5-Penta-*O*-acetyl-D-arabinitol (D-**3**)[12,18] crystallises with two independent molecules in the asymmetric unit (Fig. 4). The central carbon chains adopt the expected planar zigzag conformation which has no 1,3-interactions that involve heavy atoms. The overall conformations differ from that for D-arabinitol[19], in that O-1 in D-**3** extends the planar chain in each molecule and is *gauche* to O-2. In one of the two independent molecules of

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* Lists of observed and calculated structure amplitudes, atomic co-ordinates of all atoms, including anisotropic thermal factors for C and O, isotropic factors for H, bond distances and angles, and further information to Table I (87 pages) are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/505/*Carbohydr. Res.*, 233 (1992) 35–43.

TABLE II

Fractional positional parameters (×10^4) of carbon and oxygen atoms in **1**, **2** (modification with low melting point), D-**3**, and DL-**3** [a]

Atom	**1** (molecule I)			**1** (molecule II)			**2**		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
O-1	6351(9)	−1991(5)	6573(5)	8742(8)	−572(5)	8520(5)	5653(3)	−1296(2)	2601(2)
O-2	7208(6)	−2352(4)	8246(4)	7850(5)	−248(4)	6857(4)	8185(2)	12(2)	2200(2)
O-3	8918(6)	−3263(4)	7965(4)	6148(5)	678(4)	7054(4)	6568(2)	2106(2)	3132(2)
O-4	6543(5)	−4324(4)	7056(4)	8408(6)	1770(4)	7991(4)	3854(2)	3423(2)	1448(2)
O-5	8194(7)	−5062(5)	8235(5)	6771(6)	2463(5)	6787(5)	1558(2)	3914(2)	3257(2)
O-11	5315(8)	−2938(6)	6032(6)	9833(8)	369(6)	9005(6)	5017(3)	−2189(2)	1327(2)
O-21	6037(7)	−2897(5)	8872(5)	9056(7)	287(5)	6232(5)	9118(3)	1438(3)	386(2)
O-31	9064(7)	−3208(5)	9314(4)	6116(7)	601(5)	5709(5)	7365(5)	404(3)	5053(2)
O-41	6640(6)	−4606(5)	5763(4)	8309(7)	2037(5)	9277(4)	1846(3)	2997(3)	825(3)
O-51	8981(10)	−6111(6)	8021(6)	5934(10)	3481(16)	6962(7)	1781(3)	5446(3)	4073(3)
C-1	7178(11)	−2493(8)	6870(7)	7917(10)	−46(7)	8243(7)	5802(4)	−74(3)	1474(3)
C-2	7044(9)	−2898(7)	7622(6)	8039(9)	326(6)	7459(6)	6514(3)	826(3)	1831(3)
C-3	7824(10)	−3515(7)	7859(6)	7244(9)	941(6)	7182(6)	5634(3)	1305(3)	2935(3)
C-4	7692(10)	−4129(7)	7223(6)	7294(8)	1546(7)	7818(6)	3893(3)	2268(3)	2671(3)
C-5	8393(9)	−4780(7)	7476(7)	6577(9)	2204(7)	7542(7)	3159(4)	2951(3)	3661(3)
C-11	5417(14)	−2298(10)	6140(9)	9706(13)	−279(9)	8902(8)	5241(3)	−2298(3)	2372(3)
C-12	4563(15)	−1746(10)	5833(10)	10577(14)	−824(9)	9159(9)	5107(4)	−3512(3)	3581(3)
C-21	6658(10)	−2413(7)	8857(7)	8413(10)	−204(7)	6254(7)	9376(4)	479(3)	1404(3)
C-22	6952(11)	−1835(7)	9458(8)	8127(11)	−788(7)	5664(8)	11000(4)	−368(4)	1973(3)
C-31	9463(10)	−3120(7)	8734(7)	5663(12)	538(7)	6267(7)	7483(4)	1467(3)	4173(3)
C-32	10585(9)	−2868(7)	8754(7)	4485(10)	297(7)	6215(7)	8638(4)	2262(4)	4073(3)
C-41	6120(8)	−4561(6)	6288(7)	8828(10)	2015(7)	8762(8)	2690(4)	3727(3)	638(3)
C-42	4968(9)	−4748(7)	6213(7)	9997(10)	2204(7)	8846(6)	2644(5)	5087(4)	−477(3)
C-51	8558(12)	−5719(9)	8461(10)	6395(12)	3117(9)	6561(9)	1066(4)	5179(4)	3439(3)
C-52	8361(12)	−5960(8)	9260(9)	6612(11)	3352(7)	5775(9)	−447(4)	6161(4)	2755(4)

Atom	D-**3** (molecule I)			D-**3** (molecule II)			DL-**3**		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
O-1	−8039(5)	1801(3)	3548(1)	−8898(5)	6497(4)	5611(1)	1312(8)	3660(5)	9241(4)
O-2	−9543(4)	2991(3)	3007(1)	−7420(4)	5513(3)	4993(1)	2795(7)	4547(5)	8024(3)
O-3	−7260(4)	4605(3)	2843(1)	−9824(4)	3903(3)	4845(1)	411(6)	6140(5)	7594(3)
O-4	−7813(4)	2402(3)	2177(1)	−9297(4)	6204(3)	4220(1)	1042(6)	3827(4)	6372(3)
O-5	−5503(4)	4021(3)	2028(1)	−11545(5)	4615(3)	4029(1)	−1271(6)	5433(4)	5927(3)
O-11	−7130(6)	2437(4)	4088(1)	−10023(7)	5815(4)	6118(2)	2388(12)	5026(8)	9909(6)
O-21	−10333(4)	1357(3)	2780(1)	−6807(5)	7295(3)	4870(5)	3462(7)	2776(5)	7837(4)
O-31	−4734(4)	4625(3)	2977(2)	−12344(4)	3937(3)	4977(1)	−2096(7)	6091(5)	7857(4)
O-41	−10128(5)	2577(3)	1907(1)	−6918(6)	6151(4)	3982(2)	3432(8)	3940(6)	5968(4)
O-51	−4800(5)	5796(3)	2095(2)	−12189(6)	2823(4)	4065(2)	−1923(7)	7220(5)	6045(4)
C-1	−7246(6)	2659(4)	3347(2)	−9635(6)	5643(4)	5397(2)	521(10)	4410(8)	8711(6)
C-2	−7948(5)	2681(4)	2965(2)	−9043(6)	5783(4)	5008(2)	1171(10)	4270(7)	7966(5)
C-3	−7161(5)	3482(4)	2700(2)	−9872(6)	5036(4)	4725(2)	352(9)	4994(7)	7357(5)
C-4	−7905(5)	3530(4)	2319(2)	−9168(6)	5075(4)	4343(2)	1111(9)	4968(6)	6611(5)
C-5	−7125(6)	4308(4)	2055(2)	−9944(6)	4332(5)	4061(2)	355(10)	5697(7)	6009(5)
C-11	−7869(7)	1770(5)	3918(2)	−9131(8)	6500(6)	5973(2)	2257(12)	4076(8)	9795(5)
C-12	−8753(8)	868(5)	4094(2)	−8295(8)	7469(6)	6147(2)	3106(14)	3170(11)	10184(7)
C-21	−10630(6)	2231(4)	2921(2)	−6418(6)	6348(5)	4937(2)	3865(10)	3702(8)	7989(6)
C-22	−12208(6)	2626(5)	3028(2)	−4796(6)	5942(5)	4945(2)	5441(11)	4103(8)	8155(7)
C-31	−5940(5)	5087(4)	2954(2)	−11167(6)	3429(4)	4953(2)	−955(10)	6584(7)	7795(5)
C-32	−6194(6)	6292(4)	3035(2)	−10972(6)	2232(4)	5035(2)	−768(10)	7810(7)	7945(5)
C-41	−9041(5)	2015(4)	1991(2)	−8084(7)	6647(5)	4040(2)	2352(10)	3415(7)	6070(5)
C-42	−8891(6)	807(4)	1900(2)	−8369(7)	7841(5)	3958(2)	2110(11)	2187(7)	5922(5)
C-51	−4459(6)	4836(4)	2047(2)	−12578(7)	3769(5)	4025(2)	−2305(10)	6277(8)	5954(5)
C-52	−2857(6)	4427(4)	2011(2)	−14146(7)	4181(6)	3969(2)	−3939(10)	5862(7)	5908(6)

[a] Standard deviations in parentheses.

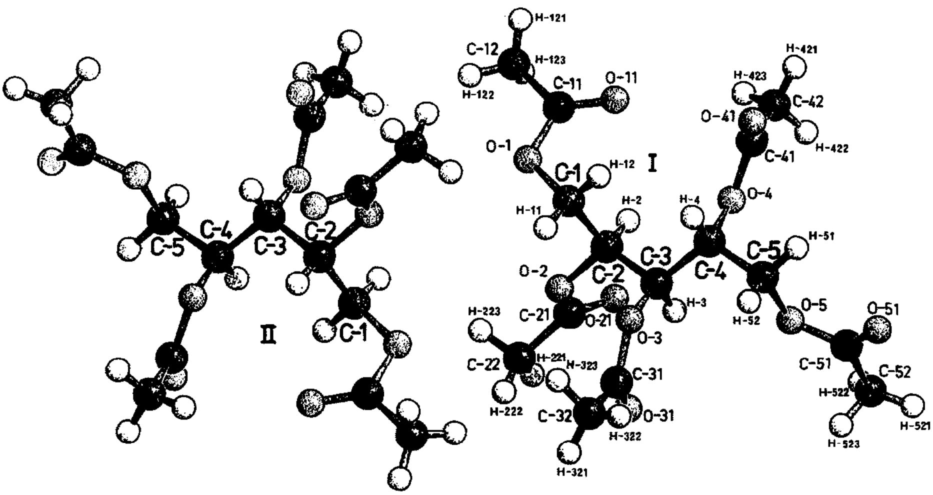

Fig. 1. SCHAKAL88[10] plot of the independent molecules of 1,2,3,4,5-penta-*O*-acetylribitol (**1**).

D-arabinitol, O-1 is *trans* to O-2, a situation which is rare in free alditols and not observed hitherto in acetylated alditols (see above).

1,2,3,4,5-Penta-*O*-acetyl-DL-arabinitol[18,20] (DL-**3**) crystallises as a racemate. In Fig. 5, a D molecule is shown, which is symmetry-related to an L enantiomer that

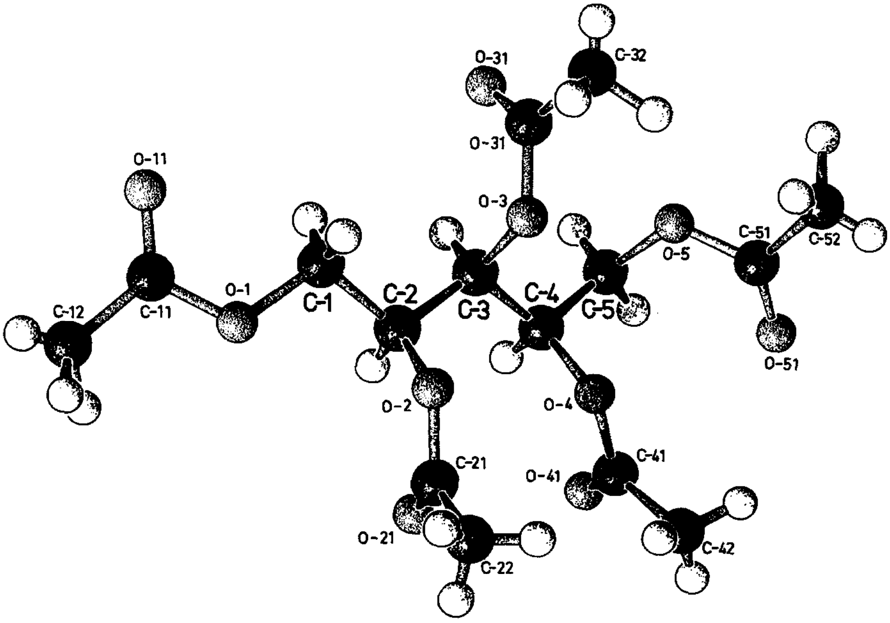

Fig. 2. SCHAKAL88[10] plot of a molecule of the modification[1] of 1,2,3,4,5-penta-*O*-acetylxylitol (**2**) with mp 65°.

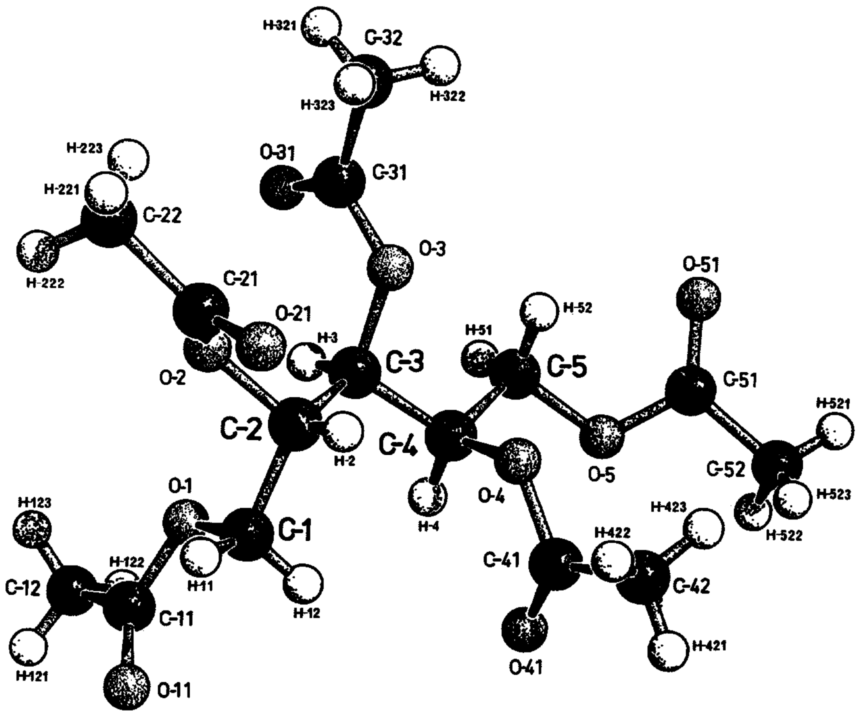

Fig. 3. SCHAKAL88[10] plot of a molecule of the modification of 1,2,3,4,5-penta-*O*-acetylxylitol (**2**) with mp 50°.

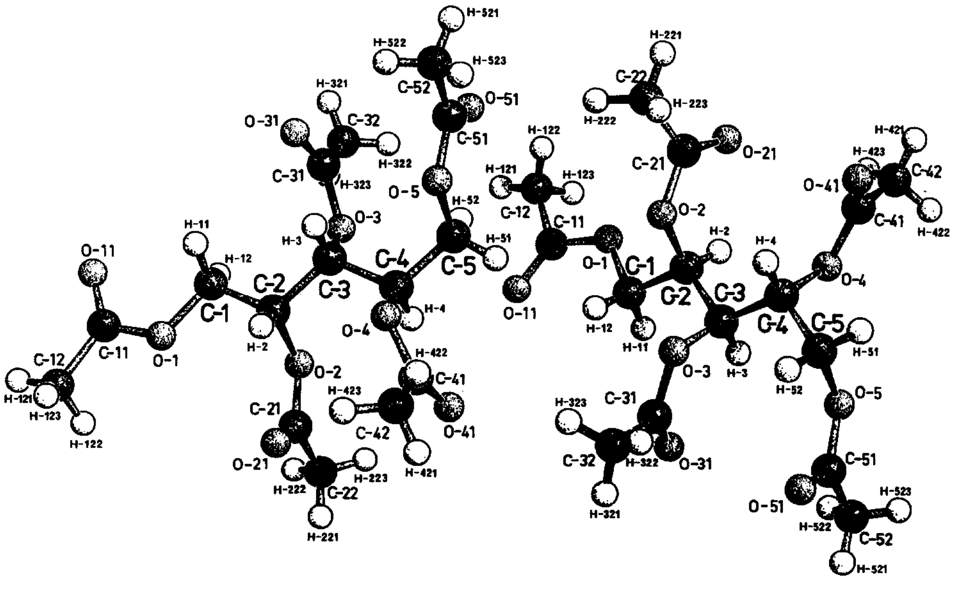

Fig. 4. SCHAKAL88[10] plot of the two independent molecules of 1,2,3,4,5-penta-*O*-acetyl-D-arabinitol (D-**3**).

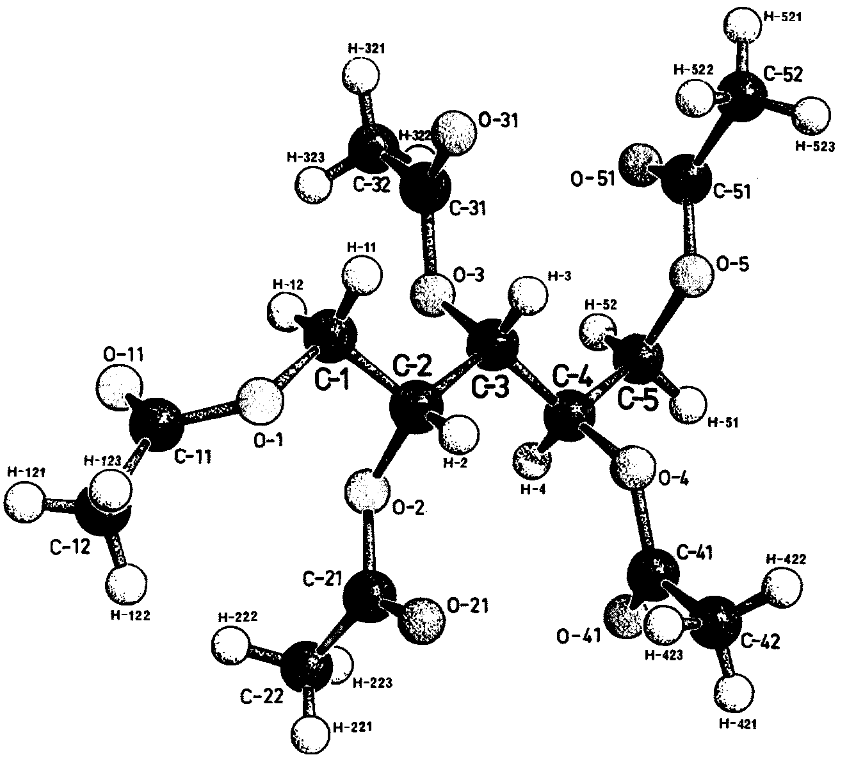

Fig. 5. SCHAKAL88[10] plot of a molecule (D) of 1,2,3,4,5-penta-*O*-acetyl-DL-arabinitol (DL-**3**). The asymmetric unit is the L enantiomer.

defines the asymmetric unit. The overall geometry of the single molecules resembles that found in D-**3** (Fig. 4) and differs from that of DL-arabinitol[21], since O-1 is *gauche* to O-2. As in one of the independent molecules in D-arabinitol[19], the molecules in DL-arabinitol[21] adopt a conformation with O-1,2 *trans*.

Thus, it is clear that the complete set of solid-state structures of the pentitol penta-acetates is much more in accord with traditional assumptions on conformations of acyclic carbohydrates (cf. the "Hassel–Ottar" effect[6]) than the related set of hexitol hexa-acetate structures[1–3]. Only for xylitol penta-acetate (**2**) with mp 65° are surprising results reported[1]. Therefore, it is concluded that the avoidance of 1,3-parallel interactions between the heavy atoms C and O (C//O and O//O, respectively) is important only in small molecules. The many violations of the "rules" concerning the stereochemistry of acyclic carbohydrates have been summarised[3].

EXPERIMENTAL

The compounds investigated were prepared by the procedures cited. The X-ray structure determinations were performed at ~ 20° and the results are given in

Table I or are deposited. Calculations of geometries were executed by using the PLATON program[22].

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