^{1}H Nuclear Magnetic Resonance Spectra and Conformations of Deoxyalditols in Deuterium Oxide

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The ^{1}H n.m.r. spectra in deuterium oxide of nine primary, monodeoxyalditols from C_3 to C_7 have been recorded at 400 MHz and the shifts and coupling constants obtained by computer simulation. The shifts and ^3J coupling constants were used to derive conformational information which supports previous results on acyclic polyols.

There is a wealth of information in the solution n.m.r. spectra and conformation of acyclic polyols, having free[1] or *O*-substituted[2] hydroxy groups, but acyclic deoxypolyols have received little attention.[1c,3] In the present work, the spectra of nine primary, monodeoxyalditols in deuterium oxide were interpreted by computer simulation; some were still very complex at 400 MHz, and the resulting shifts and coupling constants were used for conformational analysis.

Results and Discussion

Spectral Data.—Tables 1 and 2 list the proton chemical shifts and proton–proton coupling constants of the compounds studied.

As previously noted[1e] the hydroxymethyl proton with the larger ^3J value has the lower value of δ. This fact has been confirmed[4] for propane-1,2-diol.

Conformational Data.—In addition to the ^3J values derived from a Karplus-type equation[5] and used[1e] for determining the conformations of alditols, the ^3J values (Hz) in Figure 1 were also needed for the deoxyalditols. The ^3J values for MeC*H*OH–C*H*$_2$OH are as for C-1, C-2 in an alditol, MeCHOH–C*H*OH–C*H*OH–CH$_2$OH as for C-2, C-3 in a pentitol, and MeCHOH–C*H*OH–C*H*OH–CHOH ··· as for C-3, C-4 in a hexitol.

These ^3J values give the conformer distributions in Table 3 (E_g and $E_{g'}$ were averaged and 2.25 was used for both). For compounds containing a *ribo*- or *xylo*-unit, it was assumed that there were only three conformations of the chain: the planar chain having a 1,3-parallel C–O interaction (O//O) and the two conformations derived by rotation of the planar chain at (*a*) or (*b*) (Table 4) such that the O//O interaction is replaced by H//O interactions.

In the alditols, galactitol and mannitol have essentially planar carbon chains. Loss of the oxygen at C-1 leads in both cases to slightly less conformational purity (Table 3), and the purity in each case is fractionally less at the deoxy rather than the hydroxymethyl end. It is not clear which non-planar carbon-chain conformer is likely to be preferred in 1-deoxy-L-galactitol (**5**) relative to galactitol, but in deoxy-L-mannitol (**8**) the trebly

Table 1. Proton chemical shifts[a] (δ values, p.p.m.) of deoxyalditols in D_2O

Compound	1-H	2-H	3-H	4-H	5-H	6-H	7-H	Other[b]
(±)-Propane-1,2-diol (**1**)[c]	3.54	3.89	1.15					1′-H 3.45
1-Deoxy-D-arabinitol (**2**)	1.25	4.04	3.40_5	3.74	3.83			5′-H 3.66
1-Deoxy-D-ribitol (**3**)	1.21	4.01	3.60	3.68	3.83			5′-H 3.65
1-Deoxy-D-xylitol (**4**)	1.24	3.93	3.43	3.81	3.72			5′-H 3.66
1-Deoxy-L-galactitol (**5**)	1.24	4.09	3.47	3.63	3.96	3.68		6′-H 3.67
1-Deoxy-D-glucitol (**6**)	1.23	3.94	3.63	3.66	3.79	3.86		6′-H 3.68
6-Deoxy-D-glucitol (**7**)	3.74_5	3.82	3.81	3.54	3.92	1.25		1′-H 3.65
1-Deoxy-L-mannitol (**8**)	1.29	3.88	3.61	3.80	3.76	3.87		6′-H 3.68
1-Deoxy-D-*glycero*-D-*gulo*-heptitol (**9**)	1.22	3.93	3.66	3.93	3.66	3.80	3.83	7′-H 3.66

[a] Compounds (**1**), (**6**), and (**7**) referenced to external sodium 3-(trimethylsilyl)propionate. The remainder to external tetramethylsilane. [b] Primary geminal protons are distinguished by means of a prime for the proton having the larger coupling constant to the adjacent proton. [c] Lit.,[4] 1-H 3.48; 2-H 3.825; 3-H 1.10; 1′-H 3.40.

Table 2. Proton–proton coupling constants (Hz) of deoxyalditols in D_2O

Compound	$J_{1.2}$	$J_{2.3}$	$J_{3.4}$	$J_{4.5}$	$J_{5.6}$	$J_{6.7}$	Other
(**1**)[a]	4.0_5	6.5					$J_{1'.2}$ 6.6_5; $J_{1.1'}$ -11.6
(**2**)	6.6	3.0	7.5	3.0			$J_{4.5'}$ 6.5; $J_{5.5'}$ -11.5
(**3**)	6.5_5	4.6	7.8	2.8			$J_{4.5'}$ 6.7; $J_{5.5'}$ -11.8
(**4**)	6.5	5.8	3.5	4.6			$J_{4.5'}$ 7.1_5; $J_{5.5'}$ -11.5_5
(**5**)	6.6_5	1.9	9.1	1.6_5	5.1		$J_{5.6'}$ 7.7; $J_{6.6'}$ -11.5_5
(**6**)	6.4_5	7.2	1.7_5	8.4_5	3.0_5		$J_{5.6'}$ 6.3; $J_{6.6'}$ -11.8_5
(**7**)	4.0	5.4	3.1	6.5_5	6.5		$J_{1'.2}$ 6.5; $J_{1.1'}$ -11.7_5
(**8**)	6.3_5	7.8	1.5	8.5	2.6		$J_{5.6'}$ 6.0; $J_{6.6'}$ -11.8
(**9**)	6.4	5.9	4.9	2.6_5	7.9	2.9	$J_{6.7'}$ 6.4; $J_{7.7'}$ -11.7

[a] Lit.,[4] $J_{1.2}$ 4.3; $J_{1'.2}$ 6.8.

Table 3. Conformer distributions (%) in the deoxyalditols

Compound	CH$_2$OH group O_e	O_g	O_t	Planar carbon chain, except where stated
(±)-Propane-1,2-diol	53	33	14	
1-Deoxy-D-arabinitol	57	43	0	C-1–C-4 >27 <72, C-2–C-3 T_g <28; C-2–C-5 71
1-Deoxy-D-ribitol	60	42	(−2)	C-1–C-5 9. Twisted at C-2–C-3 giving O-2–C-5 planar 66. Twisted at C-3–C-4 giving C-1–O-4 planar 25
1-Deoxy-D-xylitol	55	24	21	C-1–C-5 6. Twisted at C-2–C-3 giving O-2–C-5 planar 61. Twisted at C-3–C-4 giving C-1–O-4 planar 33
1-Deoxy-L-galactitol	58	15	27	C-1–C-4 >61 <85; C-2–C-5 92; C-3–C-6 >67 <87
1-Deoxy-D-glucitol	55	44	1	C-1–C-6 7. Twisted at C-2–C-3 giving O-2–C-6 planar 78. Twisted at C-3–C-4 and C-4–C-5 giving O-5–O-3 planar 14
6-Deoxy-D-glucitol	52	35	13	C-1–C-6 11. Twisted at C-2–C-3 giving O-2–C-6 planar 54. Twisted at C-3–C-4 and C-4–C-5 giving O-5–O-3 planar 29
1-Deoxy-L-mannitol	54	51	(−5)	C-1–C-4 81; C-2–C-5 >72 <80; C-3–C-6 85
1-Deoxy-D-*glycero*-D-*gulo*-heptitol	56	44	(−1)	C-1–C-7 29. Twisted at C-2–C-3 and C-3–C-4 giving O-2–O-4 planar 48. Twisted at C-4–C-5 and C-5–C-6 giving O-4–O-6 planar 24

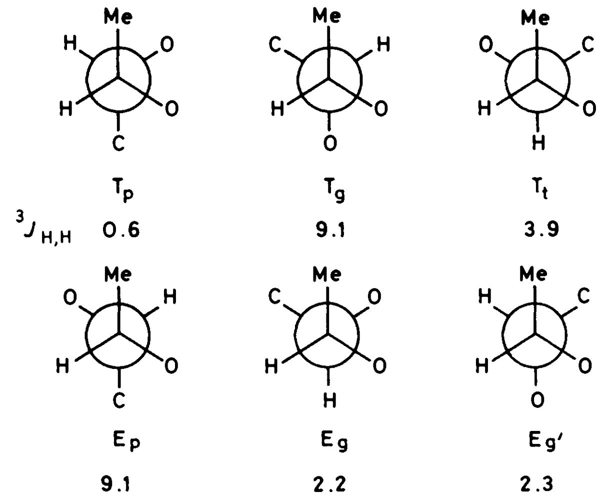


Figure 1. ^3J values (Hz) for a MeC*H*OH–C*H*OH–CHOH ··· fragment. Enantiomers of each of the forms shown for *threo*- (T) and *erythro*- (E)

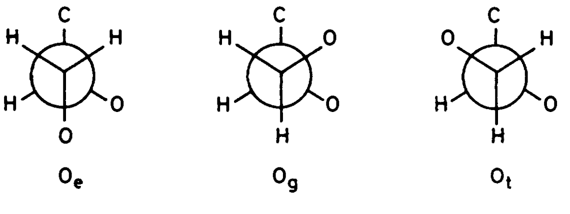
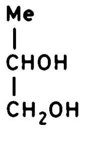
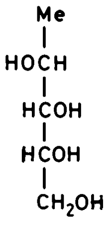


Figure 2. Hydroxymethyl group conformers. The enantiomer of each conformer has the same designation


$\mathrm{Me{-}CHOH{-}CH_2OH}$

(1)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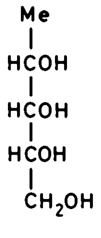
(2)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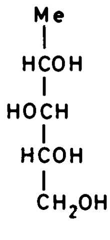
(3)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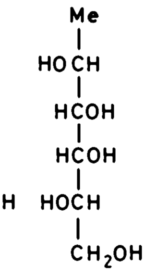
(4)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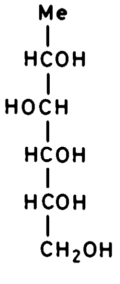
(5)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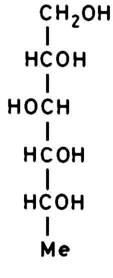
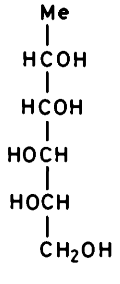
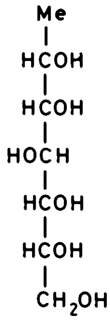
(6)


$\mathrm{CH_2OH{-}HCOH{-}HOCH{-}HCOH{-}HCOH{-}Me}$

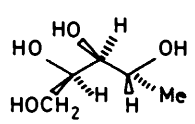
(7)


$\mathrm{Me{-}HCOH{-}HCOH{-}HOCH{-}HOCH{-}CH_2OH}$

(8)


$\mathrm{Me{-}HCOH{-}HCOH{-}HOCH{-}HCOH{-}HCOH{-}CH_2OH}$

(9)

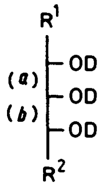
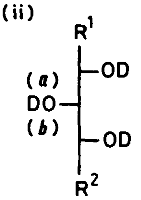


(2a)

twisted chain form[6] could be a little more preferred relative to mannitol as the C-2 methyl group suffers fewer steric interactions than does a hydroxymethyl group. However, the separation (Δ) of the proton shifts of the hydroxymethyl group in (**8**) shows that the amount of this trebly twisted form is insignificant (see later).

Interestingly, the three conformers of mannitol having a planar carbon chain and the rotamers of the hydroxymethyl groups the same, *i.e.*, O_e, O_g, or O_t, (Figure 2) are destabilised by having a symmetry number of 2, relative to the planar chain forms of (**8**). 1-Deoxy-D-arabinitol (**2**) has a relatively less planar carbon chain, relative to D-arabinitol, than (**5**) or (**8**) have to their respective hexitols. Assuming that only the planar chain and twisted chain (**2a**) forms are present, the ^3J values for the C-2–C-3 and the C-3–C-4 bonds give the ratio as 71:28,

Table 4. Polyols with *ribo-* (i) or *xylo-* unit (ii)

		Bonds (*a*) and (*b*) E_p (%)	Bond (*b*) E_p[a] Bond (*a*) E_g[a] (%)	Bond (*a*) E_p Bond (*b*) E_g[a] (%)	Σ	O_e % CH_2OD of R^2	O_g	O_t	Δ/Hz[b]
(i) 	$R^2 = CH_2OD$, R^1 = Me (**3**)	9	66	25	(100)[c]	60	42	−2	71.9
	$R^2 = CH_2OD$, $R^1 = CH_2OD$ (**10**)	8	46	46	(100)[c]	65	35	0	62.0_5
		Bonds (*a*) and (*b*) T_p (%)	Bond (*b*) T_p Bond (*a*) T_g (%)	Bond (*a*) T_p Bond (*b*) T_g (%)					
	R^1 = Me, $R^2 = CH_2OD$ (**4**)	6	61	33	(100)[c]				
	R^1 = Me, $R^2 = CHODCH_2OD$ (**6**)	7	78	14	99				
(ii) 						% CH_2OD of R^1			
	$R^1 = CH_2OD$, R^2 = Me (**4**)[d]	6	33	61	(100)[c]	55	24	21	23.0
	$R^1 = CH_2OD$, $R^2 = CH_2OD$ (**11**)	15	42	42	(100)[c]	52	29	19	28.8_5
	$R^1 = CH_2OD$, R^2 = CHODMe (**7**)	11	54	29	94	52	35	13	39.7_5
	$R^1 = CH_2OD$, $R^2 = CHODCH_2OD$ (**12**)	22	61	13[e]	96	55	38	7	45.5
	$R^1 = CHODCH_2OD$, R^2 = Me (**6**)[d]	7	14	78	99	55	44	1	74.5_5
	$R^1 = CHODCH_2OD$, $R^2 = CH_2OD$ (**12**)[d]	22	13	61[e]	96	55	44	1	70.1_5
	$R^1 = CHODCH_2OD$, R^2 = CHODMe (**9**)[d]	29 ± 6	24 ± 5	48 ± 5[f]	100	56	44	−1	68.5

[a] Oxygen extending chain. [b] At 400 MHz. [c] Sum (Σ) of rotamers = 100 used to derive populations. [d] Enantiomer. [e] From ^3J (ref. 1*e*). [f] 95% confidence limits (M. D. Pattengill and D. E. Sands, *J. Chem. Educ.*, 1979, **56**, 244).

respectively. The fact that the sum of the conformers should be 100 was not used in the calculation, so the value (99) obtained is considered as a check on the answer. Thus as the polyol length decreases in the series mannitol and galactitol, their 1-deoxy compounds, arabinitol, 1-deoxyarabinitol, erythritol, and threitol, so also does the proportion of the planar chain conformer.

The results (Table 4) for polyols containing a mono*ribo-* (i) or *xylo*-unit (ii) are compared[1e] with the appropriate alditols.

For five carbon polyols it was necessary to use the fact that the sum (Σ) of the conformers about the bonds (*a*) and (*b*) is 100, but the conformer populations for the remaining polyols were derived without using this fact, and the 1-deoxyheptitol (**9**) gave an over-determined set of equations which allowed error limits to be assigned to its values. Considering the conformation of the carbon chains in the *ribo*-series, for a constant R^2, as the size of R^1 increases, the *gauche* conformer about bond (*a*) decreases with an approximate corresponding increase in the *gauche* conformer about bond (*b*), *i.e.*, the carbon of the smaller group (Me) prefers the exoplanar position. The amount of the planar chain form is small for both (**3**) and ribitol (**10**). For D-altritol[1e] ($R^1 = CHODCH_2OD$), the assumption of only three conformers for the chain breaks down. The three *xylo*-series give a similar picture to that in the *ribo*-case, the smaller R group preferring to be *gauche*. Also, as the size of the R groups increases, it is increasingly difficult for the polyol to adopt a conformation free of non-bonded interactions, so the planar chain form increases. On this basis *meso-glycero-gulo*-heptitol ($R^1 = R^2 = CHODCH_2OD$) should have >29% with O-3//O-5 agreeing with the prediction[6] that in solution the heptitol will be mainly a mixture of the planar chain form and the enantiomeric doubly twisted chain forms. For the four series (Table 4), the smaller sized R group is always *gauche*, a result which might be reasonable on conformational grounds, but which may not always hold for other R groups.[2a,3c]

The hydroxymethyl group populations give good confirmatory support for the chain conformations (Tables 3 and 4). The O_e, O_g, and O_t hydroxymethyl group values for galactitol (53, 16, 31) and D-mannitol (54, 46, 0) were taken[1e] as characteristic for a planar chain *lyxo-* and *arabino-* configuration, respectively. The hydroxymethyl group values (58, 15, 27) for 1-deoxy-L-galactitol (**5**) show that the C-3–C-6 part of the chain is not as conformationally pure as in galactitol. In 1-deoxy-L-mannitol (**8**), the values (54, 51, −5) require slight adjustment to allow for the under-population of the O_t rotamer. Setting O_t to zero at the expense of the O_g rotamer gives an *arabino*-type hydroxymethyl ratio, confirming the essentially planar nature of the C-3–C-6 part of the chain. The reason for the negative O_t value could be that the equations used to derive the ^3J standard values are somewhat in error.

In 1-deoxy-D-ribitol (**3**), the hydroxymethyl rotamer ratios (60, 42, −2) again under-populate the O_t rotamer. Proceeding as for (**8**) gives an adjusted ratio of 60, 40, 0. If the *ribo*-unit (Table 4) had bond (*b*) 100% as the E_p rotamer, then the hydroxymethyl group (R^2) would give ratios for a planar *arabino*-type configuration. Thus in the sequence D-mannitol, 1-deoxy-D-ribitol (**3**), and ribitol (**10**) the O_t rotamer is zero in each case, and the amount of the O_e rotamer rises as that of the O_g rotamer falls. In the sequence, bond (*b*) has an increasing E_g component (with oxygen extending the chain) for which the O_g rotamer has an O//O interaction, and is therefore increasingly disfavoured. The least-squares relation between the % *arabino*-type configuration for the hydroxymethyl group, *i.e.*, bond (*b*) E_p (y) and % O_g rotamer (x) is $y = 4.18x - 92.31$. The standard deviation (s.d.) for the gradient and constant are 0.01 and 0.39, with a correlation coefficient (c.c.) of 1.0000. If the *xylo*-series for $R^1 = CH_2OD$ had bond (*a*) 100% as the T_p or 100% as the T_g rotamer, then the hydroxymethyl group would give, respectively, ratios for a planar *lyxo*-type or a planar *arabino*-type configuration. For the latter case, bond (*b*) is

Table 5. Orientation of O-ω-2 *versus* $^3J_{Me.H}$ in ω-deoxyalditols

Polyol	(8)	(9)	(6)	(7)	(1)	(4)	(3)	(2)	(5)
% O-ω-2 antiparallel ω-1-H	<19	48	21	29	33	39	66	up to 72	up to 85
$^3J_{Me.H}$	6.3_5	6.4	6.4_5	6.5	6.5	6.5	6.5_5	6.6	6.6_5

considered as replacing, in a steric sense, the ω-2 oxygen. The series therefore comprises the sequence galactitol, (4), xylitol (11), (7), glucitol (12), and mannitol. For these six polyols the amount (52—55%) of the O_e rotamer is constant, and the amount of the O_g rotamer rises as that of the O_t falls. In the sequence, bond (*a*) has an increasing T_g component, for which the O_t rotamer has a C//O interaction and is therefore increasingly disfavoured. On the other hand, the O_g rotamer increasingly relieves an O//O interaction as the T_g component rises. The least-squares relation between the % *lyxo*-type configuration for R^1, *i.e.*, bond *a* T_p (*y*) and % O_g rotamer (*x*) is $y = -3.13x + 148.0$. The s.d.s for the gradient and constant are 0.20 and 6.6, with a c.c. of 0.9918. In the *xylo*-series for $R^1 = CHODCH_2OD$, the hydroxymethyl rotamer ratio of the CH_2OD group in the R^1 group is constant and equal to that given for an *arabino*-configuration. This is because ≥77% of the chain in the R^1 + bond (*a*) is of the *arabino*-type, though some small increase in the O_e population would have been expected arising from the doubly twisted chain, in which there is steric hindrance in the O_g and O_t rotamers.

When oxygen is adjacent and antiparallel to a proton which has a *trans* ^3J coupling to an adjacent proton, this coupling increases by up to 1 Hz.[7] The $^3J_{Me.H}$ value correlates quite well with the % of oxygen antiparallel to the ω-1 proton (Table 5) and from 0 to 100% is worth *ca.* 0.4 Hz, *i.e.*, 1.2 Hz for the *trans* ^3J coupling. This effect is also seen by comparing the $^3J_{Me.H}$ values for rhamnopyranoids[8] (*ca.* 6.2) with fucopyranoids[9] (6.5 Hz), and in other ω-deoxypolyols.[3a–f]

Putting the O_g:O_t ratio for propane-1,2-diol in the Boltzmann equation gives the O_g rotamer as being 0.5 kcal mol^{-1} more stable than the O_t, which compares well with the value from 2-methoxyethyl acetate in which the rotamer with the oxygens *gauche* is more stable by 0.45 kcal mol^{-1} than the *trans*-rotamer.[10]

The relation shown for the alditols between the ^3J coupling of the more deshielded proton of a hydroxymethyl group and the adjacent methine proton *versus* the separation, Δ, of the shifts of the two protons of the hydroxymethyl group also holds for the primary deoxyalditols. Likewise[1e] the deoxyalditols obey the appropriate relation between Δ and ^3J (ω-1-H, ω-2-H). Using arguments similar to those used to relate hydroxymethyl rotamer populations to the rotamer populations of the bonds (*a*) or (*b*) in the *ribo*- and *xylo*-series, it can be shown that the separation Δ (Table 4) also relates to the rotamer populations of the nearer of the bonds (*a*) or (*b*). Thus in the sequence mannitol (Δ, 77.5 Hz), 1-deoxy-D-ribitol (3), and ribitol (10), Δ progressively decreases as the amount of bond (*b*) in the E_p state decreases, and for the series galactitol (Δ, 1.0 Hz), (4), (11), (7), (12), and mannitol, progressively increases as the amount of bond (*a*) in the T_p state decreases. Noteworthy is the series mannitol, (6), (12), and (9) in which, as previously mentioned, the hydroxymethyl ratios fail to detect the increasing amount of the E_g state of the C-ω-1–C-ω-2 bond, but the change is observable in the Δ values. Using this series suggests that 1-deoxy-D-arabinitol (Δ, 66.5) has *ca.* 25% of (**2a**), which agrees with the 28% obtained earlier from ^3J values. The Δ values also show that the amount of 1-deoxymannitol (Δ, 76.1) and 1-deoxygalactitol (Δ, 3.7) in non-planar chain states must be small.

Comparing the shifts of the deoxyalditol protons with those of the corresponding alditols (lit. values[11] used for glycerol), the deoxy protons are shielded by 2.38—2.59, the proton on C-ω-1 is deshielded by 0.10—0.20, that on C-ω-2 is shielded by 0.08—0.22 p.p.m., and protons further removed than this usually have small (±0.06 p.p.m.) differences. These values are similar (2.40—2.62, 0.02—0.11, 0.18—0.23, and ±0.07) to those given by the 6-deoxypyranoids.[8,9] These differences are useful when analysing the spectra. One factor contributing to the deshielding of the ω-1-H proton is that, in an alditol, the O_e rotamer is the main conformer of the hydroxymethyl group, and its shielding[12] gauche O/ω-1-H interaction is missing in the deoxypolyol.

The shielding of the ω-2-H proton arises from a deshielding[12] H//O interaction being partially replaced by a shielding H//H alignment. The shift of 1-deoxyribitol 4-H is the only exception to the observation that a proton more than two carbons from the methyl group has a shift within 0.06 p.p.m. of the corresponding alditol. Ribitol (**10**) has equal amounts of conformers with the chain twisted at C-2–C-3 and C-3–C-4. Thus 2-H experiences a deshielding due to an H//O-4 interaction and an antiparallel O-3[12] alternating with a deshielding H//C-5 and a shielding H/O-3 interaction. An H//O interaction is more deshielding[13] than an H//C interaction in a cyclohexane ring in aprotic solvents, and assuming this also applies in acyclic polyols in deuterium oxide, then in 1-deoxy-D-ribitol (**3**) which has 66% of the chain twisted at C-2–C-3, 2-H spends more time under deshielding influences than it does in ribitol (**10**). Relative to (**10**), 2-H in (**3**) is deshielded by 0.20 p.p.m. On the other hand, 4-H in (**3**) is shielded by 0.14 p.p.m., relative to (**10**), because it is more under the influence of the H//C and H/O interactions than it is in (**10**). In the *xylo*-series however, 4-H of xylitol (**11**) is subjected to H//O-2 and H/O-3 interactions alternating with an H//C-1 interaction and an antiparallel O-3, *i.e.*, the 4-H shifts in the two conformers are now more nearly equal, so in 1-deoxy-D-xylitol (**4**) which has 61% of the chain T_g at C-2–C-3, 4-H will not be greatly different from that in (**11**) (observed shielding 0.01 p.p.m.).

In the series 1-deoxygalactitol, 1-deoxyxylitol, and 1-deoxyglucitol the methyl proton shift remains essentially constant (δ 1.24), but there is an increasing amount of the chain at C-2–C-3 in the T_g state. The change from T_p to T_g involves the change 1-H//O-3 ⟶ 1-H//C-4, with the O-3 becoming antiperiplanar to one of the C-1–H bonds, *i.e.*, creation of a γ interaction. Therefore in terms of shift, H//O ≈ H//C + γ. In the 1,6-anhydropyranoses,[14] (in deuterium oxide) a γ interaction is observed when an equatorial proton is deshielded by 0.02—0.26 p.p.m. when an axial γ oxygen goes to an equatorial γ position. It is not known if a γ oxygen interaction is similarly deshielding in the acyclic series. In the series 1-deoxymannitol, 6-deoxyglucitol (**7**), 1-deoxyheptitol (**9**), and 1-deoxyribitol (**3**), the methyl protons are progressively shielded, δ 1.29→1.21. In the planar-chain state, there is an H//H alignment and an H//O interaction for the methyl protons, but in the twisted [for (**3**)] and doubly twisted chain [for (**7**) and (**9**)] there are H//O and H//C interactions, *i.e.*, the change involves H//H to H//C. A plot for the series of the methyl proton shift against the amount (Table 4) of the chain in the E_p state gives a straight line which extrapolates to 1.16 p.p.m. for the complete conversion H//H to H//C, *i.e.*, the H//C interaction in the *erythro*-series appears to be shielding by 0.13 p.p.m. In the 1,3-dioxanes, this change is deshielding, *e.g.*, when the *cis*-4-t-butyl-6-methyl derivative changes to the *trans*-isomer, the axial 4-H is deshielded by 0.22 p.p.m.[15] (solvent, carbon disulphide).

Experimental

^{1}H N.m.r. spectra were recorded as described before[1e] with sodium 3-(trimethylsilyl)propionate or tetramethylsilane as external reference. Where necessary, the HDO peak at δ 4.835 was used to ensure internal consistency of the spectra. Gaussian resolution enhancement was used to give a typical linewidth at half height of *ca.* 0.8 Hz. Spectra were normally fitted with an error of about 0.1 Hz (the derived shifts and coupling constants in a particular spectrum are estimated to have a similar uncertainty). The spectra were simulated as previously cited.[1e] Deoxyalditols were prepared[16] from aldoses by Raney nickel desulphurisation of the diethyldithioacetals or by borohydride reduction of the deoxyaldoses. 1-Deoxy-D-*glycero*-D-*gulo*-heptitol was obtained as a gum (lit.,[17] m.p. 124—125 °C).

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