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

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The ^{1}H n.m.r. spectra of the tetritols, pentitols, and hexitols in deuterium oxide have been recorded at 400 MHz, and the shifts and coupling constants obtained by computer simulation of the spectra. The shifts and ^3J coupling constants were used to derive conformational data which support previous results on acyclic polyols.

The wealth of information[1] on the solution n.m.r. spectra and conformation of acyclic polyols having derivatised hydroxy groups contrasts with the limited results for the unsubstituted acyclic polyols. The free alditols in solution give ^{1}H n.m.r. spectra which are not dispersed enough to be analysed, and addition of shift reagents only allows analysis of compounds which complex sufficiently to disperse the peaks.[2,3] However, some of the peaks then become broad and accurate coupling constants cannot be determined. The results from ^{13}C n.m.r. spectroscopy of the alditols in dimethyl sulphoxide[4] and in water[5] show that the free alditols, like those with protected hydroxy groups, prefer a planar carbon chain except when this results in a 1,3 parallel arrangement of two C–O bonds. The use of more powerful spectrometers now allows sufficient dispersion of the spectra of the free alditols in solution that analysis is possible, though computer simulation of the spectra is necessary as the spectra are still very second order. In the present work, the spectra of the tetritols, pentitols, and hexitols in deuterium oxide were interpreted by computer simulation 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 alditols studied. In order to solve some of the spectra, additional information was needed, and this, as well as some $^1J_{C,H}$ values, is recorded below, together with points concerning the simulation of individual polyols. ^{13}C Satellites in the ^{1}H n.m.r. spectrum yielded the following coupling constants (Hz).

[1,1,4,4-$^2H_4$]Erythritol: ^1J(C-2,H) 143, ^3J(2-H,3-H) 7.0

[1,1,4,4-$^2H_4$]-L-Threitol: ^1J(C-2,H) 142, ^3J(2-H,3-H) 4.4

[1,1,6,6-$^2H_4$]Galactitol: ^1J(C-2,H) 143, ^1J(C-3,H) 142, ^3J-(2-H,3-H) 1.5, ^3J(3-H,4-H) 9.4 (dd) (lit.,[3] 9, using non-deuteriated compound)

L-Iditol: ^1J(C-3,H) 141.5

D-Mannitol: ^1J(C-3,H) 142.

The spectrum of D-glucitol was analysed by initially solving the spectrum of the [1,1,6,6-$^2H_4$]-analogue, and then the [1,1-$^2H_2$]-analogue. The combination lines of the 1-H and 1′-H protons could not be accurately simulated without allowing ^3J(3-H,4-H) to assume an incorrectly large value (*ca.* 2.8 Hz).

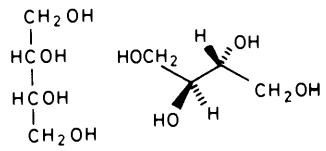
Table 1. Proton chemical shifts[a] (p.p.m.) of alditols in D_2O

	1-H	1′-H[b]	2-H	3-H	4-H	5-H	6-H	5′-H[b]	6′-H[b]
Erythritol (**1**)	3.77	3.62	3.665						
L-Threitol (**2**)	3.69	3.62	3.72						
D-Arabinitol (**3**)	3.675	3.66	3.93	3.57	3.75	3.84		3.65	
Ribitol (**4**)	3.80	3.65	3.815	3.69					
Xylitol (**5**)	3.715	3.64	3.80	3.64					
Allitol (**6**)	3.82	3.675	3.925	3.81					
D-Altritol (**7**)	3.66	3.66	3.94	3.66	3.79	3.92	3.80		3.67
Galactitol (**8**)	3.71	3.71	3.99	3.69					
D-Glucitol (**9**)	3.73	3.62	3.84	3.85	3.65	3.77	3.83		3.65
L-Iditol (**10**)	3.70	3.63	3.83	3.71					
D-Mannitol (**11**)	3.86	3.67	3.75	3.79					

[a] Downfield from external sodium 3-(trimethylsilyl)propionate. [b] Primary geminal protons are distinguished by means of a prime for the proton having the larger coupling constant to the adjacent proton.

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

	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{4,5'}$	$J_{5,6'}$	$J_{5,5'}$	$J_{6,6'}$
Erythritol (**1**)	−12.0	3.25	6.5	7.0							
L-Threitol (**2**)	−11.85	4.25	7.25	4.4							
D-Arabinitol (**3**)	−11.55	5.0	7.55	2.0	8.4	3.05		6.5		−12.0	
Ribitol (**4**)	−12.0	3.0	7.25	6.25							
Xylitol (**5**)	−11.7	4.45	6.75	4.35							
Allitol (**6**)	−11.85	3.05	7.35	5.75	6.5						
D-Altritol (**7**)	−11.75	4.7	8.0	1.9	8.25	5.0	3.15		7.4		−12.0
Galactitol (**8**)	−11.5	5.4	7.4	1.5	9.4						
D-Glucitol (**9**)	−12.0	3.55	6.55	6.0	1.7	8.25	2.95		6.3		−11.8
L-Iditol (**10**)	−11.65	4.15	7.15	4.0	5.0						
D-Mannitol (**11**)	−11.75	3.0	6.25	8.95	0.0						



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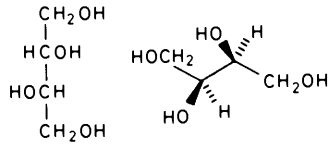

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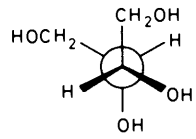

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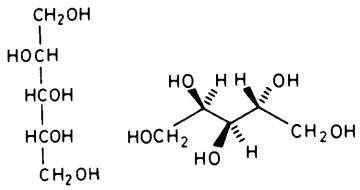

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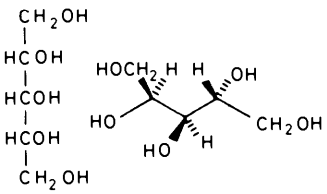

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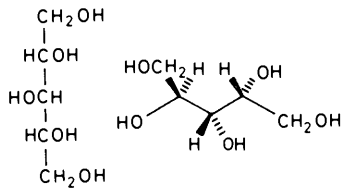

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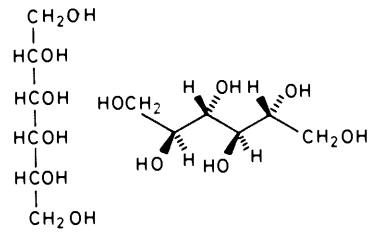

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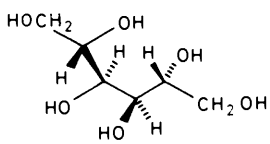
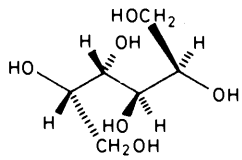


(6a)



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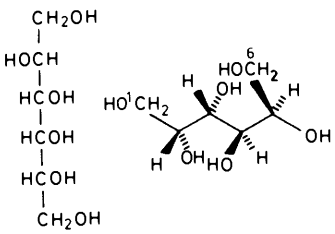

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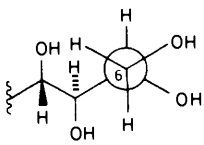

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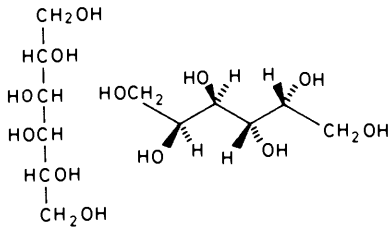

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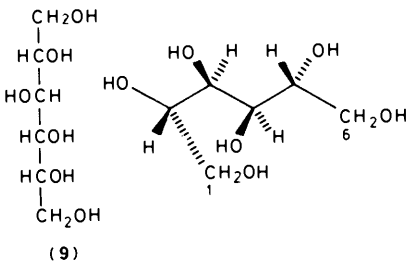

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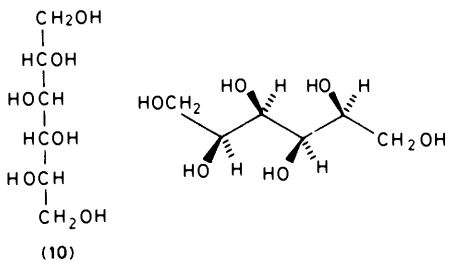

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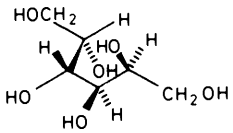

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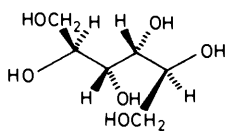

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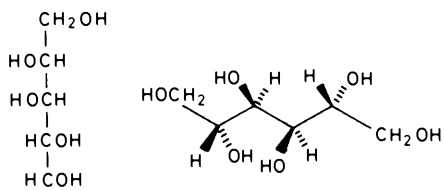

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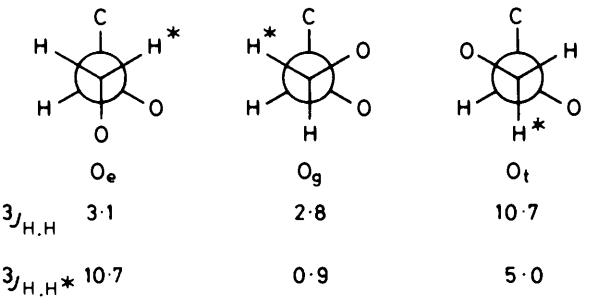

Figure 1. ^3J values in Hz

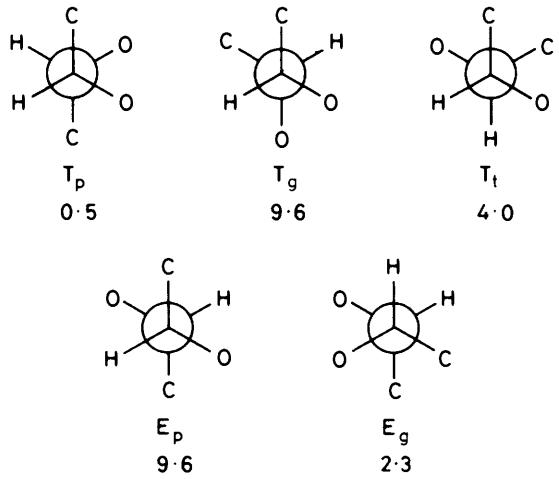

Figure 2. ^3J(2-H,3-H) values in Hz for a pentitol or hexitol. T and E = *threo* and *erythro* hydroxy groups; p = planar carbon chain. T_g and E_p have values of 9.4 for ^3J(2-H,3-H) for a tetritol and 9.7 for ^3J(3-H,4-H) for a hexitol

The spectrum of [3-^{2}H]-D-allitol could be correctly simulated but the spectrum of allitol itself not, as the programme is limited to seven spins. The values from the [3-^{2}H]-D-allitol simulation were shown to reproduce the line positions of allitol itself using the protons on C-1—C-5. The line positions in L-iditol were reproduced using the protons on C-1—C-5, in galactitol using C-1—C-4, and in D-mannitol using C-1—C-3 [^3J(3-H,4-H) = 0.0 Hz]. The spectrum of ribitol was analysed using information from its [1,1-$^2H_2$]-analogue. In no spectrum was it necessary to use a ^4J value. For each hydroxymethyl group, the proton with the larger ^3J value was at a higher field, though this characteristic was least marked in the *lyxo*-series (Figure 3).

Where comparison is possible, previous ^{1}H n.m.r. spectroscopy[2,3] has yielded ^3J values lower, on average, by 1—1.5 Hz than those in Table 2.

Conformational Data.—Using a Karplus-type equation which allows[6] for the orientation and electronegativity of substituents about the coupling protons, the ^3J values (Hz) in Figure 1 were used, where O_e (oxygen extends carbon chain), O_g (oxygens *gauche*), and O_t (oxygens *trans*) refer to the conformers of a hydroxymethyl group in a polyol. For secondary vicinal hydroxy groups the conformers have ^3J values as shown in Figure 2.

Dihedral angles of 60° are assumed in deriving these values, even though it is likely that the flexible carbon chain will cause deviations. Indeed ^{13}C n.m.r. spectroscopy of the alditols showed[4,5] that shielding due to *gauche*-oxygens (O/O) and 1,3 parallel hydrogen–oxygen (H//O) interactions were much less than in cyclohexane or pyranose rings. These ^3J values yielded the conformer distributions in Table 3, by equating the observed ^3J values to the sum of the products of the ^3J of each conformer and its amount (x) and knowing that $\Sigma x = 100$.

Table 3. Conformer distribution in the alditols

		Hydroxymethyl group (%)			Planar carbon chain (except where stated) (%)
		O_e	O_g	O_t	
Erythritol (**1**)		55	41	4	C-1—C-4 66
L-Threitol (**2**)		58	16	26	C-1—C-4 <56; C-2,C-3 T_g (**2a**) <44
D-Arabinitol (**3**)	C-1	57	17	26	C-1—C-4 >57 <84; C-2—C-5
	C-5	57	42	1	84
Ribitol (**4**)		65	35	0	C-1—C-5 8
Xylitol (**5**)		52	29	19	C-1—C-5 15
Allitol (**6**)		66	34	0	Twisted at C-2,C-3 and C-4,C-5 giving O-2—O-5 planar (**6b**) 49; twisted at C-3,C-4 (**6a**) 43; twisted at C-2,C-3 giving O-2—C-6 planar 8
D-Altritrol (**7**)	C-1	63	15	22	C-1—C-4 >60 <85; C-2—C-5 80; C-3—C-6 37 (*i.e.* O-5—C-3 planar, 63)
	C-6	66	32	2	
Galactitol (**8**)		53	16	31	C-1—C-4 >71 <89; C-2—C-5 96
D-Glucitol (**9**)	C-1	55	38	7	C-1—C-4 <40; C-2,C-3 T_g >36 <60; C-2—C-5 >66 <96; C-3—C-6 82
	C-6	55	44	1	
L-Iditol (**10**)		57	27	15	C-3,C-4 T_g (**10a**) 49; C-2,C-3 C-4,C-5 both T_g (**10b**) 26; C-2,C-3 T_g and C-3,C-6 planar 24
D-Mannitol (**11**)		54	46	0	C-1—C-4 91; C-2—C-5 100

Galactitol (**8**) and D-mannitol (**11**) have essentially planar carbon chains. The carbon chain of D-arabinitol (**3**) is somewhat less conformationally pure, presumably because it is a smaller molecule, and erythritol (**1**) and L-threitol (**2**), being smaller still, have even less planar chains. In erythritol, the chiral conformers are also favoured over the achiral ones by an entropy of mixing term.[7] Threitol has a somewhat less planar chain form (< 56%) than erythritol (66%). All C-2,C-3 rotamers of threitol are destabilised[7] by having a symmetry number of 2 when the conformations of the hydroxymethyl groups are identical. For D-altritol (**7**), the conformational purity of the C-1—C-5 chain is comparable to that in D-arabinitol. The C-3—C-6 *ribo*-portion is, as expected, twisted to relieve an O-3//O-5 interaction. D-Glucitol (**9**) also has part (C-2—C-6) of its chain of comparable conformational purity to that in D-arabinitol. The O-2//O-4 *xylo*-interaction is relieved by rotation of the chain; the amount of the conformer with O-2 extending the chain is between 36 and 60%, so the rotation caused by a *xylo*-unit seems comparable to that caused by a *ribo*-unit. Ribitol (**4**) and xylitol (**5**) are similar in that they equilibrate between a twist at C-2,C-3 and one at C-3,C-4, so removing the O-2//O-4 interaction in the planar chain form. Ribitol has 92% and xylitol 85% in this interconversion. Allitol (**6**) and L-iditol (**10**) both contain an O-2//O-4 and an O-3//O-5 interaction in the planar chain conformation. Both molecules are mixtures of conformers. They contain 43 and 49% of the chain twisted at C-3,C-4 [(**6a**),(**10a**)], 49 and 26% of the chain twisted both at C-2,C-3 and at C-4,C-5 [(**6b**),(**10b**)], and 8 and 24% of the singly twisted chain at C-2,C-3 respectively. The main iditol conformer is therefore the predicted one, but both it, the doubly twisted one and the planar form (which does not occur) are

Table 4. Group interactions (in kcal mol^{-1})[a] for allitol

Planar carbon chain	2O/O, 2O//O, 2H//O	5.6
Chain rotated so that O-2—O-5 is planar (**6b**)	4O/O, 2H//C, 4H//O	5.0
Rotation at C-3,C-4 (**6a**)	3O/O,[b] O//C, 4H//O	4.65

[a] 1 cal = 4.184 J. [b] Reduced by $RT\ln 2$ for entropy of mixing

destabilised by having a symmetry number of 2 relative to the singly twisted chain at C-2,C-3. Allitol has the doubly twisted conformer at C-2,C-3 and C-4,C-5 as its main contributor, but it also contains 43% of the singly twisted chain at C-3,C-4. Although group interactions derived [8] from six-membered rings seem too large when applied to acyclic compounds, allitol yields the values in Table 4 assuming O-1 and O-6 are in the O_e form. The three conformers have comparable energies, and although the planar carbon chain form does not in fact occur, the above may indicate why allitol contains so many C-3,C-4 twisted chains.

Turning now to a consideration of the hydroxymethyl conformer distributions (Table 3) the values for galactitol and mannitol can be taken as characteristic for a planar chain *lyxo*- and *arabino*-configuration respectively. The hydroxymethyl conformer data therefore support the case that C-1 and C-5 of D-arabinitol are associated with mainly planar *lyxo*- and *arabino*-configurations respectively. D-Glucitol C-6 also yields a planar *arabino*-arrangement. Though D-altritol C-1 is associated with a *lyxo*-arrangement, the ^3J(2-H,3-H) value shows there is some twisted form, and irrespective of whether it is T_g or T_t, the O_t conformer will decrease owing to steric interactions, and O_e will increase, as observed. A similar reasoning applies to the *ribo*-arrangement associated with C-6 (**7a**). The small planar chain fraction behaves as an *arabino*-configuration, while the main (E_g) conformer of the C-4,C-5 twisted portion only favours the O_e conformer, hence the observed C-6 conformer distribution. A hydroxymethyl group in ribitol is in a similar environment to C-6 in altritol, while xylitol C-1 has an average between the planar chain (*lyxo*) and the twist chain (*arabino*) arrangement. D-Glucitol C-1 should be mainly *arabino* type plus some *lyxo* which is associated with the planar chain portion. Allitol is like ribitol, and L-iditol should be 5:3 *lyxo*:*arabino*, giving a ratio of 53:27:19. The observed conformer distribution in L-threitol shows a *lyxo*-arrangement with a slightly enhanced O_e and a decreased O_t component. This is because in the non-planar forms, the O_t conformer is disfavoured on steric grounds. Similarly in erythritol, the *arabino*-distribution is modified in the non-planar carbon chain forms by the presence of some O_t form which can occur at one hydroxymethyl group at the expense of the O_g conformer, while the other hydroxymethyl group will prefer to be with the O_e arrangement.

Since the ^3J couplings [^3J(ω-H,ω − 1-H); ^3J(ω′-H,ω − 1-H)] between the primary protons and the adjacent proton have yielded information on conformation, it seems possible that chemical-shift data for ω-H and ω′-H may do likewise. Figure 3 shows a plot of ^3J(ω-H,ω − 1-H) values against the separation of the shifts of H-ω and H-ω′. The alditols fall into groups determined by the configuration of the three nearest oxygen atoms to the hydroxymethyl group. The ^3J(ω-H,ω − 1-H) values for the O_e, O_g, and O_t arrangements are 3.1, 2.8, and 10.7 Hz respectively, and using arguments similar to the above, it can be shown that the observed ^3J value for *arabino*- and for *ribo*-arrangements should be similar and small. Arrangements having the *lyxo*-configuration should have the largest ^3J value, with the *xylo*-type being intermediate. Interestingly, erythritol and L-threitol fall in the *ribo*- and *xylo*-regions respectively, owing to the substantial proportions of their non-planar carbon

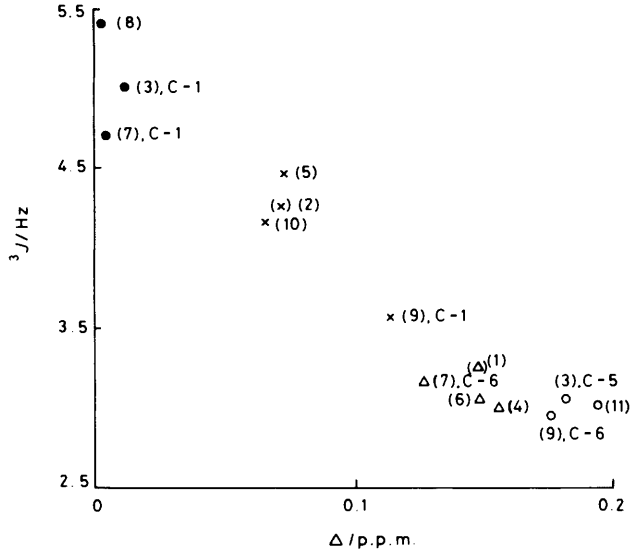

Figure 3. Plot of ^3J(ω-H,ω − 1-H) *vs.* separation Δ of primary alditol protons. ● *lyxo*-, × *xylo*-, △ *ribo*-, and ○ *arabino*-configuration. The points are identified by compound numbers

chain forms. Since Figure 3 shows that the separation of the shifts depends on the configuration and as this relates to the ^3J(ω − 1-H,ω − 2-H) value, there is a relation between ^3J(ω − 1-H,ω − 2-H) and the separation Δ. For the *arabino*–*ribo*-series (7 values) it is $^3J = 0.15\Delta - 2.87$ Hz, and for the *lyxo*–*xylo*-series (7 values), $^3J = 0.097\Delta + 1.54$ Hz. These least-squares analyses give the standard deviations of the gradients as 0.02 and 0.003, and of the constants as 1.36 and 0.073; the correlation coefficients are 0.957 and 0.9978 respectively.

Upfield shifts in ^{1}H n.m.r. spectra are related to the number of *gauche*-1,2-interactions: the '*syn*-up' rule,[9] and to the number of 1,3-parallel hydrogen (H//H) interactions.[10] Qualitatively, these effects can be seen for some of the proton shifts of the alditols. In D-arabinitol (**3**), galactitol (**8**), and D-mannitol (**11**), each 3-H has a 3-H/O interaction. The number of 3-H//H alignments are 1.32, 0.69, and 0.54 respectively, and the 3-H signal is progressively deshielded. The shifts of 2-H in D-arabinitol (**3**), galactitol (**8**), D-altritol (**7**), and allitol (**6**), and of 5-H in D-altritol (**7**) are all strongly deshielded relative to the 2-H shift of D-mannitol (**11**), or the equivalent 4-H shift of D-arabinitol. The deshielding of 2-H in D-arabinitol, galactitol, and D-altritol is due to the lack of a 2-H/O-3 interaction which is present in D-mannitol. The deshielding of 5-H in D-altritol is consistent with a high proportion of the C-4,C-5 twisted form with O-5—C-3 planar, a conformation lacking a 5-H/O-4 interaction. The deshielded 2-H signal in allitol supports a similar twisted conformation at C-2,C-3. If ribitol (**4**) had an essentially planar carbon chain, 2-H and 3-H would both be strongly shielded. In fact the observed shifts are consistent with a molecule equilibrating between a twist at C-2,C-3 and one at C-3,C-4.

In saturated six-membered rings, there is evidence that *gauche*-vicinal oxygens are slightly repulsive,[11] the effect being solvent dependent. In acyclic systems, the attractive *gauche*-effect[12–14] is reported, and there is some evidence from the hydroxymethyl group figures in Table 3 that it is operating here. For a *lyxo*-configuration the O_e:O_g:O_t ratio is 53:16:31 compared [8] with that (67:1:32) calculated by a simple additivity of group interactions derived from six-membered rings. For an *arabino*-configuration the observed and calculated values are 54:46:0 and 75:19:6. In both cases the O_e form is less than, and the O_g form more than, calculated. Although both forms involve

gauche-vicinal oxygen atoms, only the O_g form has antiparallel C–H bonds to each C–O bond, which is claimed[12] to be the requirement for the attractive *gauche*-effect. On the other hand the effect is claimed to be caused[15] by the more polar *gauche*-conformer being preferentially stabilised in polar media in comparison to the *trans*-conformer, in which case the O_e form might be as stabilised as the O_g, and the O_e distribution might be expected to be greater than that observed. An O_g conformer adjacent to *threo*-oxygens gives, for a planar carbon chain, a left-*gauche* pair of oxygen atoms followed by a right-*gauche* pair (or the enantiomeric sequence), and this is the most favourable arrangement for complexing [2] with metal ions, so part of the driving force for the complexing in acyclic systems may be the attractive *gauche*-effect.

Experimental

^{1}H N.m.r. spectra of alditols were recorded on a Bruker WH-400 spectrometer, operating on an internal lock with a probe temperature of 23 ± 2 °C. Samples (0.01—0.02 g) were examined in D_2O (1.5 ml) with sodium 3-(trimethylsilyl)-propionate (TSP) as external reference, which gave the HDO peak at δ 4.835. A few spectra were calibrated using this as standard. The computer-limited resolution was 0.29 Hz/point. Spectra were simulated[16] using the UEA NMR BASIC programme, and when necessary, the results were refined further by the UEA NMR ITERATIVE programme. 60 MHz ^{1}H n.m.r. spectra were recorded on a Varian EM-360 spectrometer, using tetramethylsilane as internal standard except where stated. The i.r. spectra were obtained on a Perkin-Elmer 257 or 457 spectrometer, using a neat film for liquids and a potassium bromide disc for solids. Methylamine chemical ionization mass spectra were obtained on a VG Micromass 12F spectrometer. Samples were introduced *via* a direct-insertion probe. Spectra were recorded at 3 or 4 kV as appropriate, at an emission current of 200 μA and an electron energy of 100 eV. The block temperature was 177 °C. When necessary the insertion probe tip was heated above 177 °C to obtain suitable volatilisation of the compound. The repeller voltage was zero, and the ion source pressure was 0.16 Torr. Under these conditions the spectrum of a sample was virtually featureless except for a prominent $(M + 32)^+$ peak.

Materials.—[1,1,4,4-$^2H_4$]-L-*Threitol.* Dimethyl L-tartrate (10.0 g), 2,2-dimethoxypropane (70 ml), and toluene-*p*-sulphonic acid monohydrate (0.5 g) were refluxed for 5 min. The mixture was neutralised with aqueous sodium hydrogen carbonate. Water and carbon tetrachloride were added, and the organic layer was washed with water and evaporated to yield crude dimethyl 2,3-*O*-isopropylidene-L-tartrate (4.0 g), mobile brown syrup; δ_H (60 MHz; neat) 1.43 (6 H, s, $Me_2C<$), 3.85 (6 H, s, ester Me), and 4.89 (2 H, s, C–H). The diester (4.0 g) in diethyl ether was reduced with lithium aluminium deuteride to yield syrupy [1,1,4,4-$^2H_4$]-2,3-*O*-isopropylidene-L-threitol (1.6 g) (lit.,[17] m.p. for non-deuteriated analogue, 49.5—51 °C); $\nu_{max.}$ 2 217 and 2 103 cm^{-1} (C–D); δ_H (60 MHz; CCl_4–$CDCl_3$) 1.43 (s, $Me_2C<$) and 4.01 (s, 2 × C–H). Hydrolysis with Amberlite IR 120(H^+) resin yielded [1,1,4,4-$^2H_4$]-L-threitol (0.5 g), m.p. 85—88 °C (from methanol–ethyl acetate) (lit.,[18] for non-deuteriated L-threitol, 88 °C); $\nu_{max.}$ 2 235 and 2 120 cm^{-1}; *m/z* 158 $(M + 32)^+$.

[1,1,4,4-$^2H_4$]*Erythritol.* Dimethyl *meso*-tartrate (9.6 g), 2,2-dimethoxypropane (55 ml), and toluene-*p*-sulphonic acid monohydrate (0.35 g) were refluxed for 9 min. Work-up as for dimethyl 2,3-*O*-isopropylidene-L-tartrate yielded syrupy dimethyl 2,3-*O*-isopropylidene-*meso*-tartrate (8.8 g); δ_H (60 MHz; $CDCl_3$) 1.43 (3 H, s, acetal Me), 1.67 (3 H, s, acetal Me), 3.81 (6 H, s, ester Me), and 4.98 (2 H, s, C–H). The diester (4.0 g) was reduced with lithium aluminium deuteride to yield syrupy [1,1,4,4-$^2H_4$]-2,3-*O*-isopropylidene-erythritol (1.9 g) (lit.,[17] m.p. for non-deuteriated analogue, 48—49.5 °C); $\nu_{max.}$ 2 218 and 2 115 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.39, 1.48 (6 H, d, Me) and 4.37 (2 H, s, C–H). Part (1.6 g) was hydrolysed with Amberlite IR 120(H^+) resin to yield [1,1,4,4-$^2H_4$]erythritol (0.75 g), m.p. 118—120 °C (lit.,[11] 119—121 °C); $\nu_{max.}$ 2 240, 2 193, and 2 122 cm^{-1}; *m/z* 158 $(M + 32)^+$.

[1,1,6,6-$^2H_4$]*Galactitol.* Diethyl 2,3:4,5-di-*O*-isopropylidenegalactarate (5.0 g),[19] δ_H (60 MHz; $CDCl_3$) 1.33 (6 H, t, CH_3CH_2), 1.45, 1.51 (12 H, d, $Me_2C<$), 4.36 (4 H, q, CH_3CH_2), and 4.6 (4 H, m, C–H), was reduced with lithium aluminium deuteride to yield [1,1,6,6-$^2H_4$]-2,3:4,5-di-*O*-isopropylidenegalactitol (3.8 g), m.p. 105—108 °C (from light petroleum, b.p. 40—60 °C–acetone) (lit.,[20] for non-deuteriated diacetal, 111 °C); $\nu_{max.}$ 2 220 and 2 100 cm^{-1}; *m/z* 298 $(M + 32)^+$; δ_H (60 MHz; D_2O; standard internal TSP) 1.50 (12 H, s, Me) and 4.22 (4 H, m, C–H); δ_H (partial spectrum, 220 MHz; D_2O; internal TSP) 4.05 (2 H, sextet, part AA'BB' system $J_{A,A'} = J_{A,B} = 7.4$, $J_{A,B'}$ 0.0 Hz, 3- and 4-H) and 4.20 (2 H, sextet, part AA'BB' system, $J_{B,B'}$ 0.0 Hz, 2- and 5-H). Part (3.0 g) was hydrolysed[21] to yield [1,1,6,6-$^2H_4$]galactitol (1.95 g), m.p. 183—185.5 °C (from water), (lit.,[22] m.p. for non-deuteriated galactitol, 188.5 °C); $\nu_{max.}$ 2 220, 2 170, 2 135, and 2 100 cm^{-1}; *m/z* 218 $(M + 32)^+$.

[1,1,6,6-$^2H_4$]-D-*Glucitol.* 2,4-*O*-Benzylidene-D-3,6-glucarolactone 1-methyl ester (m.p. 222—225 °C, lit.,[23] 233—234 °C; 1.08 g) was reduced with lithium aluminium deuteride. Amberlite IR 120(H^+) resin was added to lower the pH of the aqueous suspension to 6. The suspension was filtered (Celite), the filtrate was evaporated, and the residue was acetylated to yield [1,1,6,6-$^2H_4$]-1,3,5,6-tetra-*O*-acetyl-2,4-*O*-benzylidene-D-glucitol (1.0 g), m.p. 82—85 °C, mixed m.p. with non-deuteriated analogue was not depressed; $\nu_{max.}$ 2 240, 2 180, and 2 115 cm^{-1}; *m/z* 474 $(M + 32)^+$. Part (0.8 g) was Zemplén deacetylated and the 2,4-*O*-benzylidene acetal [m.p. 175—175.5 °C; $\nu_{max.}$ 2 220 and 2 100 cm^{-1}; *m/z* 306 $(M + 32)^+$] was hydrolysed with Amberlite IR 120(H^+) resin to yield glassy [1,1,6,6-$^2H_4$]-D-glucitol (0.21 g), co-chromatographing with non-deuteriated D-glucitol on t.l.c. and on g.l.c. (trimethylsilyl ethers on OV-17, 7 ft, at 196 °C); $\nu_{max.}$ 2 225 and 2 105 cm^{-1}; *m/z* 218 $(M + 32)^+$.

[1,1-$^2H_2$]-D-*Glucitol.* 1,5-D-Gluconolactone (0.18 g) was reduced with sodium borodeuteride, as described[24] using sodium borohydride in the presence of Amberlite IR 120(H^+) resin, to yield [1,1-$^2H_2$]-D-glucitol; $\nu_{max.}$ 2 220 and 2 110 cm^{-1}; *m/z* 216 $(M + 32)^+$.

[1,1-$^2H_2$]-D-*Ribitol.* The alditol [32%, m.p. 99—100.5 °C (lit.,[25] m.p. for non-deuteriated ribitol, 102 °C)] was prepared analogously to [1,1-$^2H_2$]-D-glucitol; $\nu_{max.}$ 2 235, 2 190, and 2 110 cm^{-1}; *m/z* 186 $(M + 32)^+$.

[3-^2H]-D-*Allitol.* 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (2.0 g) was sequentially reduced[26] with sodium borodeuteride, hydrolysed,[21] and reduced with sodium borohydride to yield [3-^2H]-D-allitol (0.27 g), m.p. 147—149 °C (lit.,[27] m.p. for non-deuteriated allitol, 151 °C); $\nu_{max.}$ 2 160, 2 130, and 2 080 cm^{-1}; *m/z* 215 $(M + 32)^+$.

L-*Iditol.* L-Sorbose (20.0 g) was reduced with sodium borohydride and the product was freed from sodium and boron in the usual way,[24] and worked up[28] to yield L-iditol (5.4 g), m.p. 67—76.5 °C (lit.,[28] 73 °C).

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