Optical Rotations and Conformations of (*S*)-Propane-1,2-diol, D-*threo*-Butane-2,3-diol and Some Alditols in Aqueous and Non-aqueous Media

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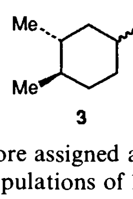
Empirical molecular rotation values for 1,2-*gauche*-substituents on a C–C unit are used additively to study the conformations of the two title diols in various solvents. Additivity breaks down for the unbranched carbon chain alditols and their primary and 2-deoxy derivatives. The deoxy compounds give characteristic rotations in water dependent on configuration, but almost independent of conformation. Likewise, alditols display almost zero rotation in water, independent of conformation, but have significant and differing rotations in non-aqueous media.

The molecular rotations, [*M*], of six-membered cyclic polyols such as pyranose sugars, cyclitols and 1,5-anhydro-compounds can be satisfactorily calculated by the method of adding the rotations due to pairwise (1,2-*gauche*) interactions of substituents.[1,2] However the method has not successfully been applied to acyclic polyols, one reason being that it is only recently that semiquantitative data are available on the conformations of such compounds. ^{1}H NMR spectroscopy showed[3] that acyclic polyol conformation was solvent dependent, and this work considers the relation between optical rotation and conformation of acyclic polyols.

Results and Discussion

(S)-(+)-*Propane*-1,2-*diol* (**1**) *and* D-(−)-*butane*-2,3-*diol* (**2**).—The effect of solvent on these two diols is shown in Tables 1 and 2. In order to relate optical rotation to conformation, the 1,2-*gauche*-interactions needed in the present work, and their shorthand notations are shown in Fig. 1. The conformers (O_e, O_g, O_t) of (*S*)-propanediol and of a hydroxymethyl group of an alditol, and the corresponding rotations [calculated from values in Fig. 1(*a*)] are also shown. While for the O/O and O/C units literature values are used, the sole literature value (60°) for a C/C unit seems too large since a mixture of 3,4-dimethylcyclohexanols[4] (**3**) had $[M]^{22}_{D}$ −16.6° (ethanol). This value corresponds to a −C/C unit. An [*M*] value for the C/C unit in Fig. 1 is therefore assigned a value of +20°. Use of the known[3] conformer populations of **1** yields the calculated [*M*] values (s.d. 6.4) of Table 1. Alternatively, the observed [*M*] values, $[M]_{\mathrm{obs}}$, can be used with the six known O_e, O_g, O_t ratios to generate [*M*] values for O/O and O/C units. A least-squares analysis gives 23 and 53°, respectively (s.d. 3.2). The O/C value is virtually that shown in Fig. 1, but that of O/O is significantly less. A plot of $[M]_{\mathrm{obs}}$ *vs.* the ^{1}H NMR separation of the shifts[3] of the hydroxymethyl protons gives an excellent straight line (correlation coefficient *r* 0.984; number of points *n* 6).



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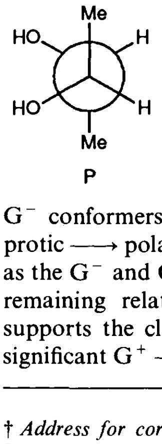
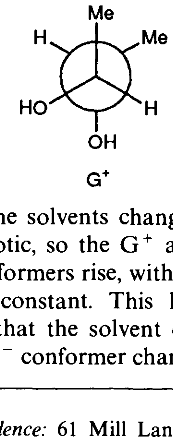
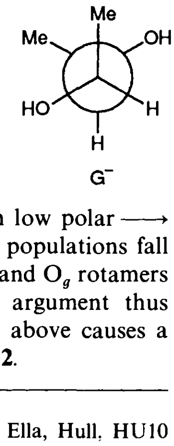
The calculated conformer populations of **2** are shown in Table 2. They are derived using $^3J_{2\text{-H},3\text{-H}}$ values[3] with the [*M*] values of Fig. 1(*a*), and knowing that the conformers add to 100%. D-Butane-2,3-diol (**2**) can be considered as the enantiomer of (*S*)-(+)-propane-1,2-diol (**1**) with the H_S proton replaced by methyl. Therefore, there is likely to be a linear relation $\{[M]_1 = -1.21\ (\pm0.13)[M]_2 - 0.22\ (\pm1.6)$: *r* 0.9593; *n* 9$\}$ between the rotations of the two diols, and on this basis the O_e, O_g, O_t conformers correspond to the G^+, P and G^- conformers. As the solvents change from low polar ⟶ protic ⟶ polar aprotic, so the G^+ and O_e populations fall as the G^- and O_t conformers rise, with the P and O_g rotamers remaining relatively constant. This line of argument thus supports the claim[3] that the solvent change above causes a significant $G^+ \longrightarrow G^-$ conformer change for **2**.



P



G^+



G^-

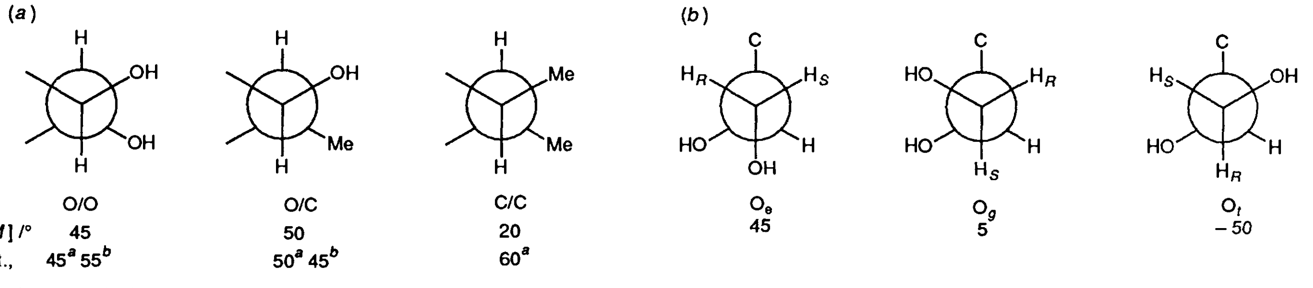


Fig. 1 Empirical molecular rotations of (*a*) units containing *gauche*-substituents, and (*b*) (*S*)-propane-1,2-diol or an alditol hydroxymethyl group. H_R, H_S identify the pro-*R* and pro-*S* protons respectively. [a] Ref. 1. [b] Ref. 2.

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Table 1 $[M]^a$ of (*S*)-(+)-propane-1,2-diol (**1**)

Solvent	$CHCl_3$ [b]	$PhNO_2$ [c]	H_2O	Pyridine [d]	1,4-Dioxane [e]	MeOH [e]	DMSO [e]	*N*-Methyl-2-pyrrolidone [f]	HMPT [e]
$[M]^{19}_{D}/°$	+22 [g]	+20	+16 [h]	+11	+11	+8	+0.5	−4	−19
$[M]_{calc}/°$	+34	— [i]	+18.5	+16	— [i]	+6	−1	— [i]	−16

[a] 1.4–3.3 g 100 cm^{-3} $[M]$ values accurate to ±3%. [b] Ordinary grade, used as received. [c] 'Analar' grade, used as received. [d] 'Analar' grade, dried. [e] Redistilled and dried. [f] Ordinary grade, dried. [g] Lit., +23° (N. Shieh and C. C. Price, *J. Org. Chem.*, 1959, **24**, 1169). [h] Lit., +16° (B. T. Golding, D. R. Hall and S. Sakrikar, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1214). Other lit. values: +3° (EtOH) (E. Baer and H. O. Fischer, *J. Am. Chem. Soc.*, 1948, **70**, 609) and +7° (Et_2O) (S. Corsano and E. Mincione, *J. Chem. Soc., Chem. Commun.*, 1968, 738). [i] Value unknown as rotamer populations not determined.

Table 2 $[M]^a$ and conformational data for D-(−)-butane-2,3-diol (**2**)

Solvent	$PhNO_2$ [c]	PhCN [b]	CCl_4 [c]	$PhCO_2Et$ [b]	PhH [b]	Et_3N [d]	$CHCl_3$ [b]	$(ClCH_2)_2$ [b]	$MeNO_2$ [e]
$[M]^{19}_{D}/°$	−22	−22	−20	−20	−18	−17	−17	−15	−12
P,G^-,G^+ [j]			6,6,88		13,11,76		10,11,79		

Solvent	MeCN [g]	Pyridine [d]	Sulpholane [e]	$MeCO_2Me$ [b]	Et_2O [f]	$H_2C(OMe)_2$ [b]	$(MeOCH_2)_2$ [b]	H_2O	Me_2CO [b]
$[M]^{19}_{D}/°$	−11	−11	−11	−11	−10	−10	−9	−9 [h]	−8.5
P,G^-,G^+ [j]		15,17,68						20,20,60	

Solvent	1,4-Dioxane [e]	HOAc [e]	Pr^iOH [b]	DMF [e,i]	MeOH [e]	$(EtO)_3PO$ [b]	*N*-Methyl-2-pyrrolidone [f]	DMSO [e]	HMPT [e]
$[M]^{19}_{D}/°$	−8	−7	−6	−5	−5	0	+0.5	+1	+13
P,G^-,G^+ [j]								18,30,52	20,42,38

[a] 2.5–3.0 g 100 cm^{-3} (but 0.5 g for CCl_4) $[M]$ values accurate to ±3%. [b,c,e,f] As in Table 1. [d] Redistilled. [g] HPLC grade, used as received, [h] Lit., −10° (R. E. Reeves, *J. Am. Chem. Soc.*, 1947, **69**, 1836). [i] *N,N*-Dimethylformamide. [j] The sets of three numbers are % of P, G^- and G^+ conformers respectively.

Alditols.—It is well-known that these compounds have almost zero $[M]_{obs}$ values in water (Table 6). Of the C_4 to C_7 alditols,[5] the largest magnitude $[M]_D$ value is six (for iditol). Indeed it has been long practice[6] to add a complexing agent to try and improve the values. Use of the $[M]$ values of Fig. 1 with the known[7,8] conformer populations of the alditols, gave calculated $[M]$ values for the alditols, but agreement with the observed values was poor. For example, D-*glycero*-D-*galacto*-heptitol (D-perseitol) (**4**) had a calculated $[M]$ of +18, whereas $[M]_{obs} = -2°$. For unbranched carbon chain polyols which can adopt a relatively strain-free planar chain, the proportion of the planar chain conformer increases as does the chain length.[9] Of the heptitols, D-perseitol is the only one to have a relatively strain-free planar chain,[10] and therefore it should have the largest amount of planar chain conformer of the C_4 to C_7 alditols. ^1H NMR spectroscopy confirmed that it had an essentially planar chain. It is thus surprising that it gave poor agreement between $[M]_{calc}$ and $[M]_{obs}$. The problem of perseitol can be presented a second way. In D-mannitol, which has an essentially planar chain, the hydroxymethyl group is adjacent to a D-*erythro*-unit and the O_e, O_g, O_t ratio,[7] taken with the values in Fig. 1(*b*), yields an $[M]_{calc}$ of +27° in water. This group contribution is termed $+m$. Similarly, for a planar chain with a D-*threo*-unit next to a hydroxymethyl group, the $[M]_{calc}$ of the hydroxymethyl group contribution is +10° in water. This situation occurs in galactitol, and is termed $+g$. The $[M]_{calc}$ contribution (e) of a D-*erythro*-unit in a planar chain is zero (due to symmetry), while the contribution ($+t$) of a D-*threo*-unit is O/O − 2O/C (= −55°). The 1- (**5**) and 7-deoxy-D-perseitols (**6**) should also have planar chains. Not only are the m and g values inconsistent when calculated from the data in Fig. 2, but using the $[M]_{calc}$ values of m and g fails to reproduce any of the $[M]_{obs}$ values. It seems clear that the method of pairwise interactions fails to predict the rotation of alditols. The fact that 7-deoxy-D-perseitol (**6**) has on $[M]_{obs}$ value significantly different from zero, suggests that the deoxy group is reponsible for the rotation. This idea is developed in Table 3 where the observed rotations of monodeoxyalditols are grouped according to the constitution of the two hydroxy groups nearest the deoxy group.

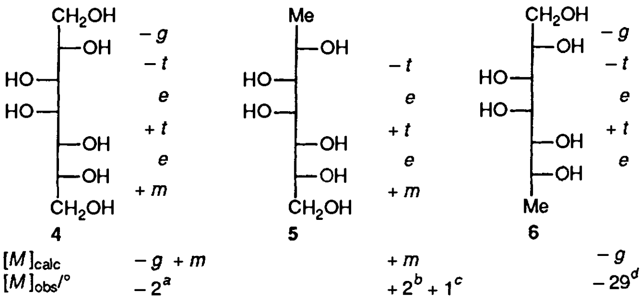
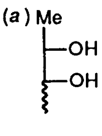
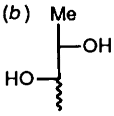
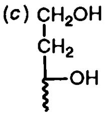


Fig. 2 Molecular rotations in water of D-perseitol (**4**) and its 1-(**5**) and 7-deoxy derivatives (**6**). [a] Ref. 5. [b] E. Zissis, N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, 1950, **72**, 3882. [c] E. Votocek and F. Valentin, *Collect Czech. Chem. Commun.*, 1938, **10**, 77. [d] A. Gateau-Olesker, A. M. Sepulchre, G. Vass and S. D. Gero, *Tetrahedron*, 1977, **33**, 393.

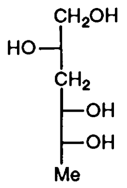
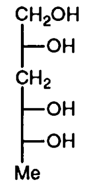
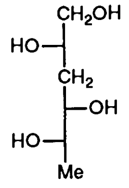
In Table 3, the rotation of primary deoxyalditols of type (*a*) is significantly positive, with the planar chain 1-deoxy-D-*glycero*-L-*manno*-heptitol (7-deoxy-L-perseitol) showing the highest value. 1-Deoxy-L-mannitol also has a planar chain, but presumably slightly less. All but one of the remaining polyols of type (*a*) have twisted chains, and their rotations are lower and lie between 13 and 18°. The spread of $[M]$ values for the type (*b*) primary deoxy compounds is less than for the type (*a*) and there is no obvious difference in rotation for planar chain

Table 3 Monodeoxyalditols grouped according to the constitution of the two hydroxy groups nearest the deoxy group

		$[M]^{b}_{\text{obs}}$
(*a*) 	1-Deoxy-D-*glycero*-L-*manno*-heptitol[a]	$+27^{c}$ $+25^{d}$
	1-Deoxy-L-mannitol	$+21^{e,5b}$
	1-Deoxy-D-allitol	$+18^{e,f,5b}$
	1-Deoxy-D-erythritol	$+18^{g}$
	1-Deoxy-D-gulitol	$+17^{5b}$
	6-Deoxy-L-altritol	$+16^{e,h}$
	1-Deoxy-L-*glycero*-L-*talo*-heptitol	$+16^{e,i}$
	1-Deoxy-D-ribitol	$+14^{e,5b}$ $+18^{e,j}$
	1-Deoxy-L-lyxitol	$+14^{e,j}$
	1-Deoxy-D-*glycero*-D-*gulo*-heptitol	$+13^{k}$
	av. excluding first entry	+17
(*b*) 	1-Deoxy-D-glucitol	$+7^{l}$
	1-Deoxy-L-*glycero*-D-*gluco*-heptitol	$+4^{m}$
	1-Deoxy-D-*glycero*-D-*galacto*-heptitol (**5**)	$+2^{n}$ $+1^{o}$
	1-Deoxy-D-galactitol	$+2^{p}$
	1-Deoxy-D-xylitol	0^{q}
	1-Deoxy-L-*glycero*-D-*galacto*-heptitol	0^{r}
	1-Deoxy-L-arabinitol	$-1^{e,s}$ -2^{l}
	1-Deoxy-L-iditol	$-2^{e,5b}$
	1-Deoxy-L-alditol	$-4^{e,5b}$
	av.	+1
(*c*) 	2-Deoxy-L-*lyxo*-hexitol	$-30^{e,t}$
	2-Deoxy-D-*erythro*-pentitol	-29^{5b}
	2-Deoxy-L-*arabino*-hexitol	$-29^{e,5b}$
	2-Deoxy-D-*ribo*-hexitol	-16^{u}
	av. excluding last entry	−29

[a] Enantiomer of **6**. [b] Na–D line; water. [c] E. Fischer and O. Piloty, *Ber. Dtsch. Chem. Ges.*, 1890, **23**, 3827. [d] B. Coxon and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, 1964, **86**, 922. [e] Enantiomer measured. [f] Ref. 5(*b*) incorrectly states D-isomer. [g] I. R. McKinley, Thesis, London, 1972. [h] N. K. Richtmyer, L. C. Stewart and C. S. Hudson, *J. Am. Chem. Soc.*, 1950, **72**, 4934. [i] B. Lindberg and H. Meier, *Acta Chem. Scand.*, 1962, **16**, 543. [j] V. Bilik, L. Petrus and J. Zemek, *Chem. Zvesti*, 1978, **32**, 242. [k] E. Zissis, N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, 1951, **73**, 4714. [l] G. N. Bollenback and L. A. Underkofler, *J. Am. Chem. Soc.*, 1950, **72**, 741; H. Muller and T. Reichstein, *Helv. Chim. Acta*, 1938, **21**, 251. [m] Ref. *d*, Fig. 2. [n] Ref. *b*, Fig. 2. [o] Ref. *c*, Fig. 2. [p] T. G. Bonner, E. J. Bourne, D. Lewis and L. Yuceer, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1323. [q] S. David, B. Estramareix, J-C. Fischer and M. Therisod, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2131. [r] E. Votocek, *Collect Czech. Chem. Commun.*, 1938, **10**, 273. [s] E. Zissis and N. K. Richtmyer, *J. Am. Chem. Soc.*, 1954, **76**, 5515. [t] W. G. Overend, F. Shafizadeh and M. Stacey, *J. Chem. Soc.*, 1951, 2062. [u] T. Bando and Y. Matsushima, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 593.

Table 4 $[M]_{\text{D}}$ of some 3-deoxyhexitols in water

			
$[M]_{\text{obs}}$ mono-3-deoxy	-52.5^{a}	-27^{a}	$-78^{a,b}$
$[M]_{\text{calc}}$	−36	−10	−79
$[M]_{\text{obs}}$	-45^{c}	-17^{c}	-64^{d} $-66^{b,e}$

[a] Ref. 5(*b*). [b] Enantiomer measured. [c] H. B. Wood, Jr. and H. G. Fletcher, Jr., *J. Org. Chem.*, 1961, **26**, 1969. [d] T. G. Bonner, D. Gibson and D. Lewis, *Carbohydr. Res.*, 1980, **78**, 243. [e] P. Szabo and L. Szabo, *Carbohydr. Res.*, 1967, **4**, 206.

Table 5 Rotations/° of some dideoxyalditols in water

	$[M]^{a}_{\text{obs}}$	$[M]_{\text{calc}}$
D-Butane-2,3-diol	-9^{b}	−2(*b*) = −2
L-*arabino*-Pentane-2,3,4-triol	$+7^{c}$	(*a*) + (*b*) = +18
1,6-Dideoxy-L-mannitol	$+34^{d}$	2(*a*) = +34
1,6-Dideoxy-L-altritol	$+19^{d,e}$	(*a*) + (*b*) = +18
1,6-Dideoxy-L-iditol	0^{f}	2(*b*) = +2
2,6-Dideoxy-D-*ribo*-hexitol	-50^{g}	−(*a*) + (*c*) = −46
D-*threo*-2,5-Dideoxyhexitol	$+20^{h}$	−2(*c*) = +58

[a] Na–D line. [b] Table 2. [c] Ref. *g*, Table 3. [d] E. Zissis and N. K. Richtmyer, *J. Am. Chem. Soc.*, 1952, **74**, 4373. [e] Enantiomer measured. [f] Ref. 5(*b*). [g] H. Lichti, M. Kuhn and A. von Wartburg, *Helv. Chim. Acta*, 1962, **45**, 868. [h] N. K. Kochetkov and A. I. Usov, *Tetrahedron*, 1963, **19**, 973.

[1-deoxy-D-galactitol and **5**] or twisted chain compounds. 2-Deoxypolyols of type (*c*) have a significant negative rotation, but that of 2-deoxy-D-*ribo*-hexitol is somewhat different from the other three examples.

The position concerning 3-deoxyalditols is less clear. Table 4 gives $[M]_{\text{obs}}$ values for some 1,4-dideoxyhexitols and $[M]_{\text{calc}}$ for the corresponding 4- (*i.e.*, 3-) deoxy compound after subtracting the effect of the primary deoxy group using the average values given in Table 3. The $[M]_{\text{calc}}$ values give fair agreement with $[M]_{\text{obs}}$. It is not clear from the data in Table 4 whether $[M]$ for 3-deoxyalditols depends on the configuration or conformation of the chain about the deoxy group. In Table 3, the rotation was determined only by the two nearest hydroxy groups to the deoxy group. This criterion clearly fails for 3-deoxy compounds having an *erythro*-arrangement of hydroxy groups at C-2 and C-4, since this arrangement, having a plane of symmetry, would yield an inactive compound, and the second entry in Table 4 shows this to be incorrect. Also syrupy L-*threo*-3-deoxypentitol[11] has $[M]$ −17° (H_2O). Its enantiomer will therefore have an $[M]$ value different in sign and magnitude from the 3-deoxy compounds in Table 4 having a D-*threo*-arrangement of hydroxy groups at C-2 and C-4 (entries 1 and 3). Therefore the $[M]$ values of 3-deoxyhexitols must be determined by at least three hydroxy groups. Use of the average values of types (*a*), (*b*) and (*c*) in Table 3 shows reasonable agreement, except for the last entry, between the $[M]_{\text{obs}}$ and $[M]_{\text{calc}}$ values for some dideoxypolyols (Table 5). A confirmation of the rotation for the last entry—a syrup, would be useful.

Considering now the effect of different solvents on $[M]_{\text{obs}}$ for the acyclic polyols, Table 6 shows that not only does a given compound have different rotations in different solvents, but different polyols can have significantly different rotations in the same solvent. Thus non-aqueous solvents can usefully be used to characterise polyols and to differentiate their enantiomers. Use of the $[M]$ values in Fig. 1 for the alditols with known conformer populations[3] in non-aqueous solvents again yielded poor agreement between $[M]_{\text{calc}}$ and $[M]_{\text{obs}}$, *e.g.*, D-mannitol in hexamethylphosphoric triamide (HMPT) had $[M]_{\text{calc}}$ −24 (assuming a planar chain) against $[M]_{\text{obs}}$ −39°. The rotary power of the polyols (Table 6) does not always seem to be related to any obvious solvent property, *e.g.*, $[M]$ of D-mannitol is zero in water, +10 in dimethyl sulphoxide (DMSO) and −39° in pyridine and HMPT.

One unresolved aspect of this work is when the pairwise interactions of *gauche*-substituents are or are not additive. For propanediol, the O_g population remains relatively constant with solvent change, so that the amount of O_e or O_t will be linear with $[M]_{\text{obs}}$ if the pairwise interactions are additive. Linearity is in fact observed. Similarly, for butanediol, the P conformer is relatively constant (6–20%) with solvent change, and the amount of G^- conformer is linearly related to $[M]_{\text{obs}}$, again with additivity of pairwise interactions. However, it seems that

Table 6 $[M]^{a}_{\text{obs}}/^{\circ}$ of some polyols in different solvents

Solvent	H_2O	MeOH[e]	DMSO[e]	Pyridine[d]	HMPT[e]	Other
L-Threitol	−5	+12	+13	+25	+37	+13[b]
D-Arabinitol	0	−12	−8	−31	−40	—
D-Altritol	+5	—	−7	−31	−38	—
D-Glucitol	−3	−3	+10	−17[c]	+1	—
L-Iditol	−6	+14	+11.5	+30	+35	—
D-Mannitol	0	—[f]	+10	−39[g]	−39	−7[h]
D-*glycero*-D-*galacto*-Heptitol (**4**)	−2	—[f]	+20	—[f]	+2	—
D-*glycero*-L-*galacto*-Heptitol	+5	—[f]	−15	−18[g]	−35	—
D-*glycero*-D-*gluco*-Heptitol	−2	—[f]	+12	−11	−3	—
D-*glycero*-L-*gulo*-Heptitol	+2	—	−7	−50	−42	—
D-*glycero*-D-*manno*-Heptitol	+4	—[f]	+16	−35	−33	—
1-Deoxy-L-galactitol	−2	+9	+18.5	+23	+30	—
1-Deoxy-D-glucitol	+7	−2	+7	−13	−25	—
1-Deoxy-L-mannitol	+21	+21	+12	+49.5	+21	—
2-Deoxy-D-*arabino*-hexitol	+27	+26	+44	+15[i]	+13	—
2-Deoxy-D-*lyxo*-hexitol	+30	+10[j]	+16	−8	+9	—
L-*erythro*-Hexane-1,2,3-triol	−12	−22	−19	−10.5	−49	−23, −23, −20, −17[k]

[a] 1.0–1.3 g 100 cm^{-3}; 19 °C, $[M]$ values accurate to within ±5% but most of the rotations in water are lit. values, mainly from ref. 5. [b] EtOH (R. K. Ness, H. G. Fletcher, Jr. and C. S. Hudson, *J. Am. Chem. Soc.*, 1951, **73**, 4759). [c] Lit., −15 °C (H. H. Strain, *J. Am. Chem. Soc.*, 1934, **56**, 1756). [d,e] As in Table 1. [f] Too insoluble. [g] Saturated solution (0.8–0.9 g 100 cm^{-3}). [h] DMF (dimethylformamide) (von R. Kuhn and H. Grassner, *Justus Liebigs Ann. Chem.*, 1957, **610**, 122). [i] Lit., +18 °C (M. L. Wolfrom, M. Konigsberg, F. B. Moody and R. M. Goepp, Jr., *J. Am. Chem. Soc.*, 1946, **68**, 122. [j] Lit., +20 °C (Ref. *t*, Table 3). [k] 1,4-Dioxane, acetone, DMF and MeCN respectively.

additivity has broken down in threitol which, like the other unbranched chain alditols has almost zero rotation in water, yet D-threitol can be considered as butane-2,3-diol (**2**) with a hydrogen of each methyl group substituted by a hydroxy group.

Conclusions

Semiquantitative conformer populations are given for D-butane-2,3-diol in various solvents. The amount of intermolecular hydrogen bonding between solvent and diol increases as does the rotation of the diol in the solvent, and so rotation values may serve as an easily determined measure of the hydrogen bond acceptor power of the solvent.

The rotation of a 1- or 2-deoxyalditol, $[M]_{\text{deoxy}}$, in water, is given by eqn. (1) where $[M]_{\substack{\text{deoxy}\\ \text{group}}}$ is the rotation due to the deoxy

$$[M]_{\text{deoxy}} = [M]_{\substack{\text{deoxy}\\ \text{group}}} + [M]_{\substack{\text{rest of}\\ \text{chain}}} \qquad (1)$$

group and $[M]_{\substack{\text{rest of}\\ \text{group}}}$ is the rotation due to the remainder of the chain. This latter term is essentially zero in water. In non-aqueous media, alditols have significant rotations and there is presently insufficient data to determine whether eqn. (1) still holds. The status of 3-deoxyalditols is unclear, and may be resolved when rotations of the 3-deoxyheptitols are available.

Experimental

Samples were usually dissolved in 1.2–1.3 cm^3 of solvent and the rotations were measured in a 1 dm cell using a Perkin-Elmer 241 polarimeter operating on the Na–D line.

Materials.—L-Iditol,[7] heptitols[8] and monodeoxyalditols[9] were prepared as previously. Reduction of D-talose gave D-altritol. The synthesis of hexane-1,2,3-triol is to be published. All other polyols and diols **1** and **2** were commercially available.

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