Co-operative Intramolecular Hydrogen Bonding in Glucose and Maltose

John C. Christofides and David B. Davies,*
Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX

SIMPLE ^{1}H n.m.r. measurements of glucose, maltose, and some of their derivatives in dimethyl sulphoxide solution confirm the inter-residue 2'-OH ··· 3-OH hydrogen bond in maltose and reveal the presence of weaker intra-residue hydrogen bonds between vicinal hydroxy groups in both glucose and maltose. Co-operative stabilisation of intra-residue hydrogen bonding is provided by the participation of the anomeric hydroxy group in glucose and by the inter-residue 2'-OH-3 ··· OH hydrogen bond in maltose.

Intramolecular hydrogen-bonding properties of α-1→4 glucosides are important for understanding the structural and conformational properties of such molecules as maltose, malto-oligomers, amylose, and cyclodextrins (Figure 1). The presence of intramolecular hydrogen bonding for α-1→4 glucosides in [$^2H_6$]Me_2SO solution has long been demonstrated by application of i.r. and n.m.r. measurements,[1] and analysis of a number of n.m.r. parameters (chemical shifts, coupling constants, and temperature dependence of chemical shifts) indicated[2] that the 2'- and 3-OH groups on adjacent residues were involved in intramolecular hydrogen bonding and that 3-OH is the likely donor and 2'-OH the acceptor group. This conformational model was confirmed by recent ^{1}H and ^{13}C SIMPLE n.m.r. measurements on cyclodextrin,[3,4] ^{13}C SIMPLE n.m.r. of maltose,[4] and by ^{1}H n.m.r. studies of methyl maltoside,[5] where it was shown that intramolecular hydrogen bonding between hydroxy groups is manifested by isotope-shifted hydroxy proton[3,5] and corresponding methine carbon resonances[4] for molecules with partially deuteriated hydroxy groups observed under conditions of slow exchange (*e.g.* in [$^2H_6$]Me_2SO solution). In addition to the isotope effects corresponding to the intramolecular hydrogen bond a smaller isotope effect was observed for the 3'-OH resonance of methyl maltoside,[5] suggesting the presence of hydrogen bonding between neighbouring hydroxy groups in one residue. Similar, but more extensive, hydrogen bonding has been observed in other disaccharides such as sucrose and its derivatives.[6–8]

In the present work a detailed study of isotope effects observed for the hydroxy proton resonances of glucose and maltose and some of their derivatives shows that the relatively strong inter-residue hydrogen bond stabilises an intra-molecular hydrogen-bond network which extends to both the reducing and non-reducing residues. The extent and nature of the hydrogen-bonding network were investigated by comparison of the isotope effects observed in maltose with those for the appropriate reducing and non-reducing monomer residues. Observation of very small deuterium-induced isotope shifts for the hydroxy proton resonances of glucose in [$^2H_6$]Me_2SO solution indicates the presence of weak intramolecular hydrogen bonds between hydroxy groups on neighbouring carbon atoms. The origin of the isotope effects observed for each hydroxy group of glucose has been investigated by SIMPLE ^{1}H n.m.r. measurements of the 1-*O*- and 3-*O*-methyl derivatives.

Experimental

All carbohydrates (except the methyl β-D-maltopyranoside, a gift from Tate and Lyle Group Research and Development Laboratory) were obtained commercially (Sigma Chemical Co.) and used without further purification. Samples were prepared as described previously.[7] 500 MHz ^{1}H N.m.r. measurements were made on a Brucker AM-500 spectrometer (N.I.M.R., London) and spectra were calculated with resolution enhancement at a data resolution of *ca.* 0.1 Hz per point.

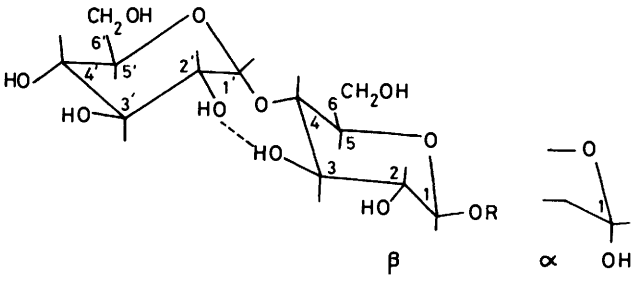
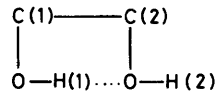


Figure 1. Structure and atom numbering of the α-1→4 glucobiose unit of β-maltose (R = H) and methyl β-D-maltoside (R = CH_3)

Results and Discussion

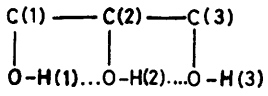
(1) *Patterns of Isotope Effects on Hydroxy Proton Resonances.*—Deuterium substitution of hydrogen-bonded hydroxy protons leads to the observation of isotope-shifted signals for the hydroxy resonances of the unsubstituted hydroxy groups.[3,8] When both the protio and deuterio molecules are present, resonances from both molecules can be observed under conditions of slow exchange, and the isotope shift is easily measured from the spectrum. The appearance of the hydroxy proton resonance observed under conditions of partial deuteriation (SIMPLE n.m.r.) depends on the number of isotope effects, their signs, and relative magnitudes; it also depends on the deuteriation ratio (OH:OD) of the molecules and the magnitude of the spin coupling constant with the appropriate vicinal methine proton. Patterns of isotope effects for hydroxy proton resonances are described for the one and the two isotope effect case.

One isotope effect. One isotope effect is observed for each hydroxy proton resonance when two hydroxy groups are involved in a hydrogen-bond interaction as shown in Scheme 1. Signals for 1-OH correspond to 2-OH isotopomers (i) and (ii) (labelled H and D, respectively) whereas 2-OH signals correspond to 1-OH isotopomers (i) and (iii). The relative intensities (*I*) of isotopomer hydroxy proton signals for 1- or 2-OH are directly proportional to the OH:OD ratio. Negative isotope effects correspond to signals shifted to lower frequencies on substitution with the heavier isotope whereas positive isotope effects correspond to signals shifted to higher frequencies.



Isotopomer			
	H	H	(i)
	H	D	(ii)
	D	H	(iii)
	D	D	(iv)

Scheme 1.



Isotopomer			
	H	H	$I(HH)=p(OH)^2$
	H	D	$I(HD)=I(DH)$
	D	H	$=p(OH).p(OD)$
	D	D	$I(DD)=p(OD)^2$

Scheme 2.

Two isotope effects. The case where the hydroxy group being considered (2-OH) is hydrogen-bonded to two different hydroxy groups (1- and 3-OH) is shown diagrammatically in Scheme 2 together with the four possible isotopomers (HH, HD, DH, and DD, reflecting the state of deuteriation of 1- and 3-OH). The relative intensities (I) of the isotope-shifted resonances of the 2-OH signal corresponding to each species depends on the deuteriation ratio OH : OD as shown in Scheme 2 in terms of the relative population (p) of the protio and deuterio forms

Ignoring the effect of proton spin-coupling constants, which effectively doubles the pattern of resonances, the appearance of the 2-OH resonances for different signs and magnitudes of the two isotope effects is shown in Figure 2 at two deuteriation ratios. If the magnitudes of the two isotope effects are different, four lines are expected corresponding to the different isotopomers, whereas three lines are observed if the magnitudes of the two isotope effects are equal. Designation of lines in each multiplet to the four isotopomers depends on the relative signs of the isotope effects. Resonance signals with similar distributions of intensities are expected for isotope effects with either the same signs (Cases 1 and 4) or different signs (Cases 2 and 3). Examples of signals exhibiting two isotope effects of the same sign (both negative) and of opposite signs are found in this work.

(2) *Intra-residue Hydrogen Bonds in Glucose Monomers.—Methyl* α-D-*glucopyranoside and* 3-O-*methyl*-D-*glucose.* The 500 MHz SIMPLE ^1H n.m.r. spectrum of the hydroxy proton resonances (OH : OD *ca.* 1 : 1) of 1-*O*-methyl α-D-glucopyranoside in $[^2H_6]Me_2SO$ solution is shown in Figure 3.

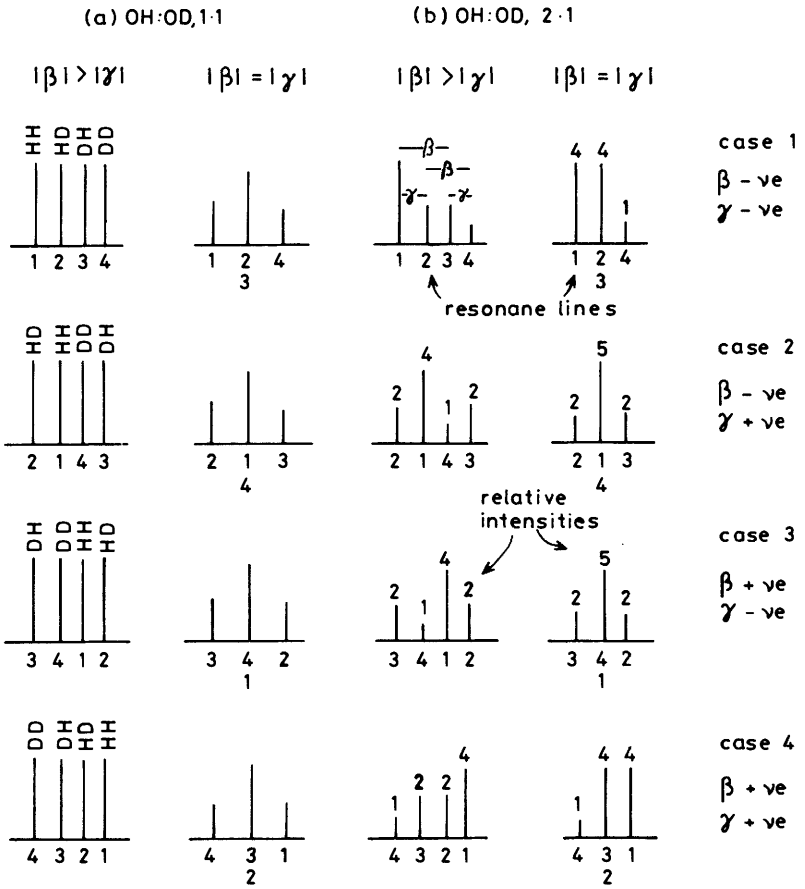


Figure 2. Dependence of the number of lines and their relative intensities on the signs and magnitudes of two isotope effects (labelled β and γ) at OH:OD ratios of (**a**) 1:1 and (**b**) 2:1

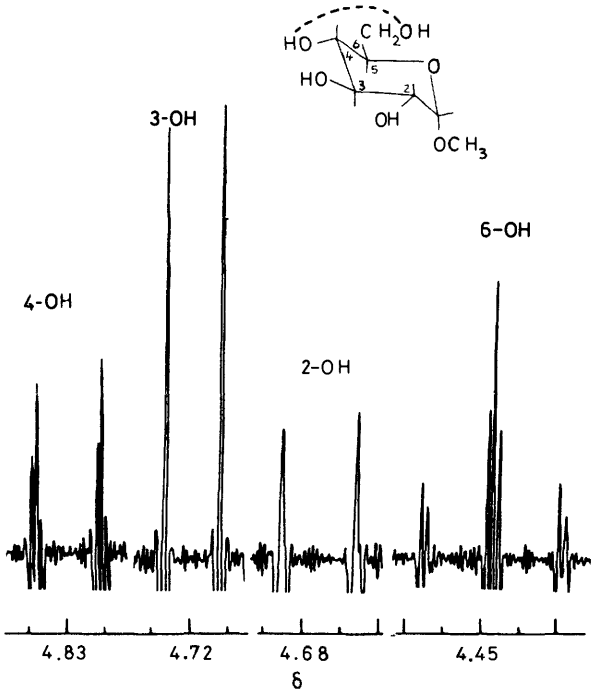


Figure 3. 500 MHz SIMPLE ^1H n.m.r. spectrum of the hydroxy proton resonances of 1-*O*-methyl α-D-glucopyranoside in $[^2H_6]Me_2SO$ solution at 295 K at a deuteriation ratio OH:OD *ca.* 1:1

Assignment of the hydroxy signals has previously been reported.[9] No isotope effects are observed for the 2- and 3-OH resonances whereas one small isotope effect is observed for both the 4- (-7×10^{-4} p.p.m.) and 6-OH ($+10 \times 10^{-4}$ p.p.m.) resonances. Similar small isotope effects are observed for the 4- and 6-OH signals of 3-*O*-methyl-D-glucose and so the origin of the effect on 4-OH is shown to be deuterium substitution of 6- rather than 3-OH; the origin of the isotope effect on 6-OH is most likely due to deuterium substitution of 4-OH.

The small isotope effects observed for the 4- and 6-OH signals are consistent with the existence of a very weak hydrogen bond between these hydroxy groups as shown for the structure of methyl α-D-glucopyranoside in Figure 3. Such hydrogen bonds between 4- and 6-OH have been observed in the solid state in the crystal structures of *N*-acetyl-α-D-galactosamine[10,11] and planteose,[12,13] and in carbon tetrachloride solutions of substituted glucopyranosides by i.r. spectroscopy.[14]

α-D-*Glucose*. The 500 MHz ^1H n.m.r. spectrum of the hydroxy proton resonances of D-glucose consists of signals from both α- and β-anomers though only those for the α-anomer assigned previously[9] are shown in Figure 4(a). The 1α-OH signal exhibits a small long-range coupling constant ($^4J_{2\text{-H},1\text{-OH}}$ *ca.* 1 Hz).[9] One positive isotope effect is found for each of the 2-, 3-, and 6-OH signals ($+22$, $+20$, $+9 \times 10^{-4}$ p.p.m., respectively) whereas the 4-OH resonances exhibits one resolved positive isotope effect ($+15 \times 10^{-4}$ p.p.m.) and a second smaller effect (sign not determined) that appears as line broadening when compared with other signals in the same spectrum or to the signals of the normal protio form.

The isotope effect observed for 2-OH in α-glucose ($+ 22 \times 10^{-4}$ p.p.m.) is thought to be due to intramolecular hydrogen-bond formation with the anomeric 1-OH rather than 3-OH since methyl substitution at O(3) does not prevent observation of this isotope effect for 2-OH whereas it does for methyl substitution at O(1). For 3-*O*-methyl-D-glucose it was also

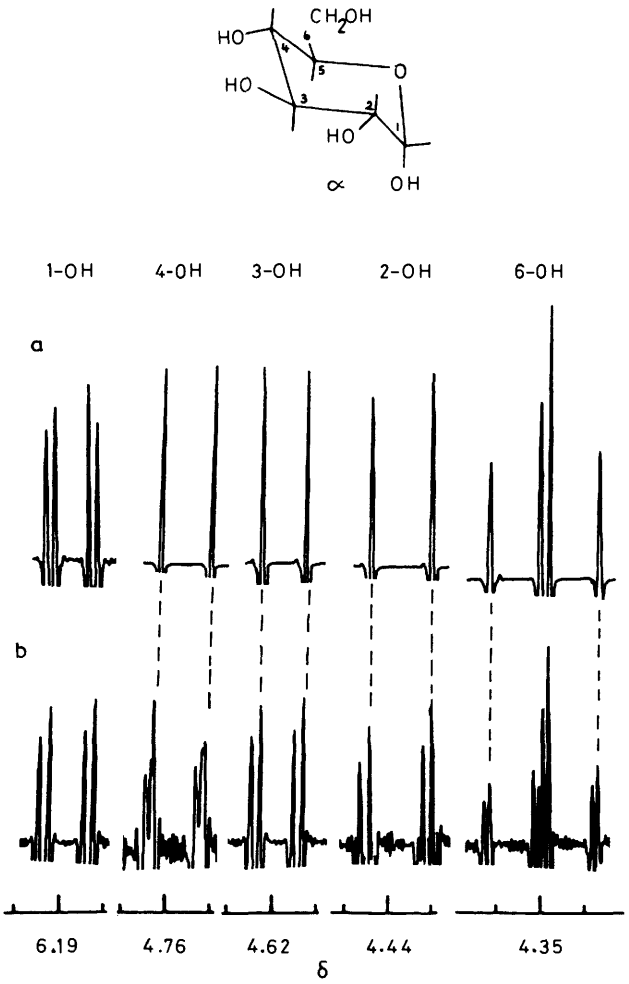
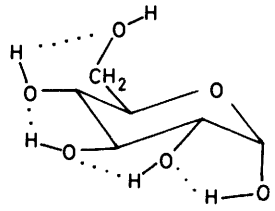


Figure 4. 500 MHz ^1H N.m.r. spectrum of the hydroxy proton resonances of α-D-glucose in $[^2H_6]Me_2SO$ solution at 295 K at different deuteriation ratios (a) OH:OD, 1:0; (b) OH:OD *ca.* 4:3



Scheme 3.

shown that isolation of the 2-OH ··· 1-OH hydrogen bond is manifested by a small resolved isotope effect on 2-OH, but no isotope effect is observed for 1-OH, which suggests that the latter effect is very small. Differences in the magnitudes of isotope effects for two hydroxy groups involved in a hydrogen bond[7,15] could explain the fact that no isotope effect is observed for 1-OH and also the fact that only one isotope effect is resolved for 2- and 3-OH, whereas two should be observed for each hydroxy group involved in hydrogen bonding to two neighbouring hydroxy groups. This view is supported by our measurements of n-dodecyl glucoside in $[^2H_6]Me_2CO$ solution, where the magnitudes of the isotope effects are larger (Table) and hydrogen bonding between neighbouring hydroxy groups is manifested as isotope effects on all signals. The isotope effects observed for glucose are consistent with the hydrogen-bond Scheme 3 in which a weak hydrogen-bond network extends

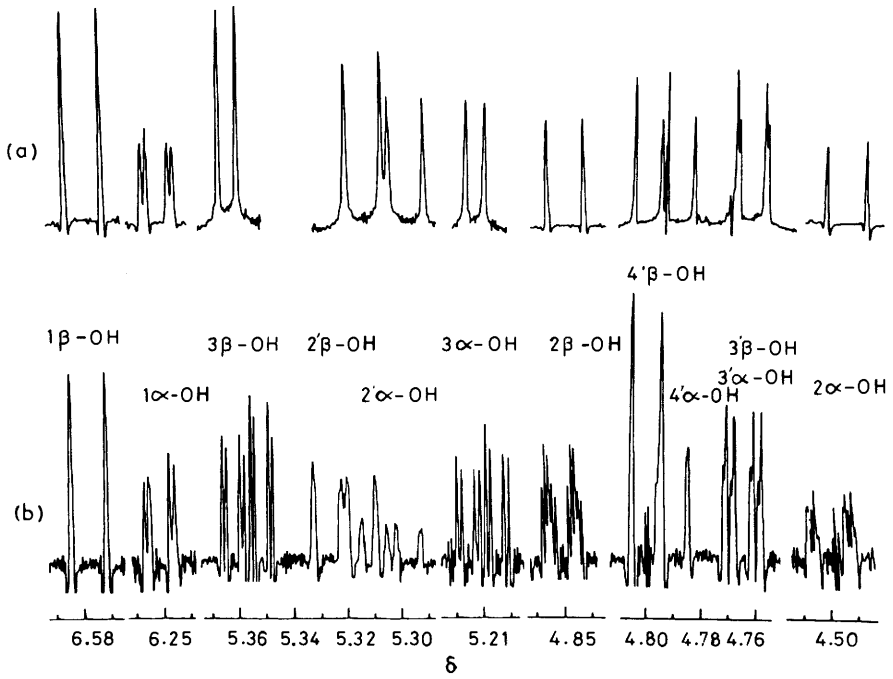


Figure 5. 500 MHz ^{1}H n.m.r. spectrum of the hydroxy proton resonances of maltose in [$^2H_6$]Me_2SO solution at 310 K at different deuteriation ratios (a) OH:OD, 1:0; (b) OH:OD *ca.* 1:1

round one side of the molecule from the anomeric hydroxy group, through 2-, 3-, and 4-OH to the primary 6-OH.

Scheme 3 for hydrogen bonding in glucose does not imply which OH groups are the predominant donor or acceptor groups or that the hydrogen bonds form all of the time. Indeed the hydroxy groups exhibit considerable flexibility and adopt a range of conformations not significantly different from those for free rotation as shown by the magnitudes of vicinal coupling constants ^3J(HCOH) which only vary in the range 4.5—6.0 Hz, whereas the value for free rotation is *ca.* 5.3 Hz.[16] The observed isotope effects are the weighted averages of those magnitudes for hydroxy groups acting either as donors or acceptors in hydrogen bonding, whereas no contribution to the isotope effect is expected for hydroxy groups in conformations where no hydrogen bonding occurs. The small isotope effects observed for hydroxy groups of glucose in [$^2H_6$]Me_2SO solution therefore correspond to extremely weak intramolecular hydrogen bonds that, previously, have only been inferred from i.r. measurements of glucose derivatives in carbon tetrachloride solution.[14,17]

Effect of anomeric hydroxy groups. The difference in patterns of isotope effects for the 2-, 3-, and 4-OH signals of α-D-glucose compared with methyl α-D-glucopyranoside highlight the importance of the anomeric hydroxy group in stabilising co-operative hydrogen bonding between 2-, 3-, and 4-OH. As a consequence of the anomeric effect it is found that the anomeric hydroxy group makes a stronger hydrogen-bond donor compared with the other hydroxy groups for molecules in the solid state.[18,19] The hydrogen bond between the anomeric 1-OH and the neighbouring 2-OH in glucose must polarise the 2-OH bond sufficiently for a hydrogen bond to form with 3-OH (and thence to 4-OH) whereas the absence of the anomeric hydroxy group in methyl α-D-glucopyranoside means that no hydrogen bonding is observed for 2- and 3-OH. These results extend the pioneering work of Lemieux and Pavia[20] who observed many years ago that the solvent can strengthen intramolecular hydrogen bonding involving a hydroxy group by polarisation of the O–H bond. The importance of the co-operative effect in stabilising hydrogen-bond structures is demonstrated by observations on carbohydrates in the crystal state by neutron diffraction measurements, where it is found that most hydroxy groups take part in chains of hydrogen bonds that run through the crystal lattice.[21–23] It is also found in the crystal state that anomeric hydroxy groups make strong hydrogen-bond donors and are often found at the origins of chains of hydrogen bonds.

(3) *Effect of Inter-residue Hydrogen Bonds in α-1→4 Glucosides.—Maltose and methyl β-D-maltoside.* The 500 MHz ^{1}H spectrum of the secondary hydroxy groups of maltose [Figure 5(a)] shows that both anomers are present in the ratio α:β *ca.* 1:2. The signals were assigned in this work by selective decoupling and two-dimensional COSY n.m.r. spectroscopy. Signals for 6- and 6'-OH are not shown due to extensive overlap of second-order resonances.

The 500 MHz SIMPLE ^{1}H n.m.r. spectrum of the hydroxy proton resonances (OH:OD *ca.* 1:1) of both α- and β-maltose [Figure 5(b)] shows that isotope effects are exhibited for all signals except the anomeric hydroxy group. Resolved isotope effects are observed for 2-(>2), 3-(2), 2'(>1), and 3'-OH(>1) signals of both α- and β-anomers; smaller isotope effects leading to line broadening are observed for the 2-, 3'-, and 4'-OH signals (Table).

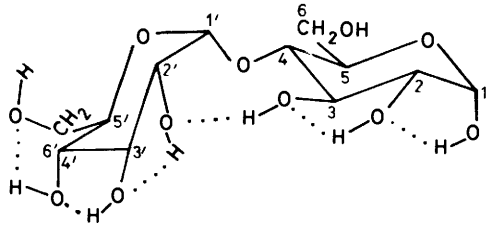
The number of isotope effects observed for each hydroxy signal corresponds to the minimum number of hydroxy groups with which it participates in hydrogen-bond formation. In general terms the isotope effects observed for the hydroxy signals of maltose may be rationalised by the presence of a relatively strong inter-residue 3-OH • • • 2'-OH hydrogen bond which stabilises an intramolecular hydrogen-bond network between hydroxy groups on neighbouring carbon atoms in both the reducing and non-reducing residues as shown in Scheme 4.

The relatively large isotope effects observed for 2'- ($+104\alpha$, $+90\beta \times 10^{-4}$ p.p.m.)* and 3-OH (-103α, $-104\beta \times 10^{-4}$ p.p.m.) are similar to those observed for the same signals in cyclo-

* No significance should be given to the difference between the isotope effects for α- and β-maltose because of the relatively larger error limits ($\pm 10 \times 10^{-4}$ p.p.m.) in their magnitudes caused by the presence of another small, unresolved isotope effect on 2'-OH.

dextrin[3] and correspond to the isotope effects transmitted through the 3-OH (donor)···2-OH (acceptor) inter-residue hydrogen bond. As found previously for sucrose,[6,7] the relatively strong inter-residue hydrogen bond stabilises a hydrogen-bond network in the non-reducing glucose residue which is manifested as resolved isotope effects on 3′-OH ($+28 \times 10^{-4}$ p.p.m.) and line broadening isotope effects for 2′-, 4′-, and 6′-OH. The small chemical-shift difference between the 3α- and 3′β-OH signals of maltose [Figure 5(b)] prevents complete analysis of their isotope effects and so SIMPLE ^{1}H n.m.r. measurements have also been made for methyl β-D-maltoside in [$^2H_6$]Me_2SO solution (Figure 6). Except for the 2- and 3-OH resonances (see below) the number, magnitudes, and signs of isotope effects for the hydroxy proton resonances of methyl β-D-maltoside are similar to those observed for maltose. The 3′-OH resonance (Figure 6) reveals the presence of two isotope effects of opposite signs which suggests that the hydroxy group may be acting both as a donor and acceptor of a hydrogen bond as shown in Scheme 4.

The inter-residue hydrogen bond also stabilises a hydrogen-bond network for the reducing residue of maltose manifested by the small isotope effect on 3-OH (-20×10^{-4} p.p.m.) and at least two isotope effects on 2-OH as shown by the presence of five lines rather than the four required for two isotope effects; no isotope effects are observed for the 1-OH signal as noted previously for glucose and 3-*O*-methylglucose. Although the



Scheme 4.

Table. Magnitudes ($\times 10^{-4}$ p.p.m.) and signs of isotope effects[a]

	1-OH	2-OH	3-OH	4-OH	6-OH
α-D-Glucose	*b*	+22	+20	+15[c]	+9
3-*O*-Methyl-α-D-glucose	*b*	+25		*c*	*c*
3-*O*-Methyl-β-D-glucose	*b*	+25		*c*	*c*
Methyl α-D-glucopyranoside		*b*	*b*	−7	+10
n-Dodecyl β-D-glucopyranoside[d]		−12, −35	−21, −40	−22	+17
α-Maltose *GG*	*b*	50[e]	−103, −20		*b*
GG		+104[c]	28	*c*	*c*
β-Maltose *GG*	*b*	50[e]	−104, −20		*b*
GG		+90[c]	28	*c*	*c*
Methyl β-D-maltoside *GG*		+14, −14	−99		*b*
GG		+144[c]	+32, −17		*c*

[a] 500 MHz ^{1}H N.m.r. measurements in [$^2H_6$]Me_2SO solution (*T* 295 K) at a data resolution of <0.1 Hz per point. Error limits $\pm 2 \times 10^{-4}$ p.p.m. [b] No isotope effect observed. [c] Isotope effect observed by increase in linewidth ($< 10 \times 10^{-4}$ p.p.m.) under conditions of partial deuteriation. [d] 500 MHz ^{1}H N.m.r. measurements in [$^2H_6$]Me_2SO solution (*T* 294 K) at a data resolution of 0.1 per point. [e] Sum of three isotope effects.

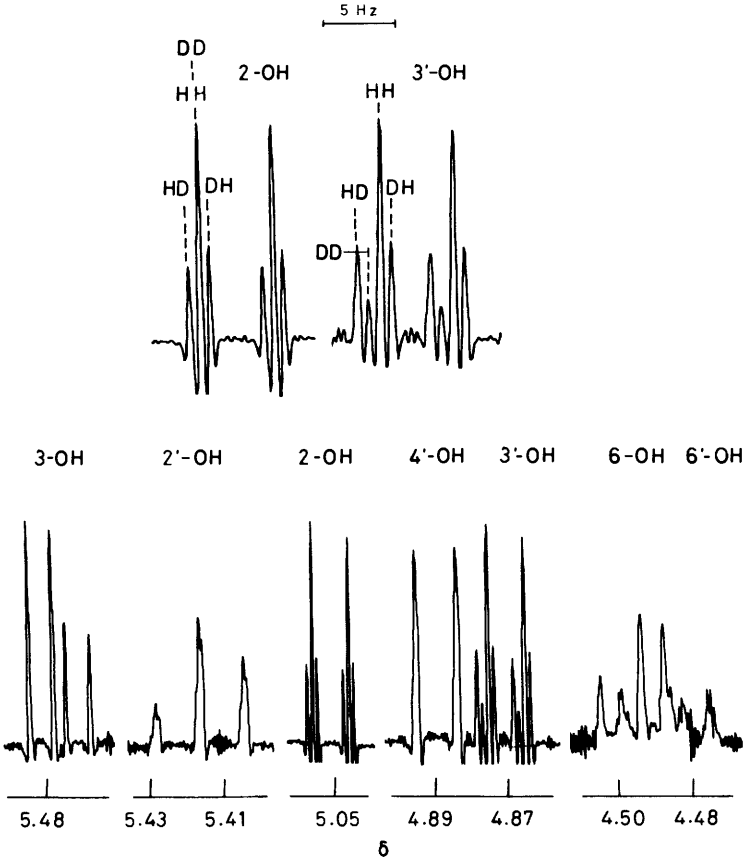


Figure 6. 500 MHz ^{1}H n.m.r. spectrum of the hydroxy proton resonances of methyl β-D-maltoside (OH:OD, *ca*1:1) in [$^2H_6$]Me_2SO solution at 295 K. The 2-OH signal shows two isotope effects of opposite signs and of the same magnitude, whereas 3′-OH shows two isotope effects of opposite signs and of different magnitudes

origin of the additional isotope effect on 2-OH is not understood at present, it is known that one of the isotope effects is due to 1-OH because the corresponding 2-OH signal in 1-*O*-methyl β-D-maltoside (Figure 6) only shows two isotope effects. The origin of the additional isotope effect for 2-OH is unlikely to be due to a long-range effect from a hydroxy in the same residue because the only possible candidate is 6-OH, which is eight bonds away. Instead it is tentatively proposed that the additional isotope effect might be transmitted through two hydrogen bonds, *i.e.* H/D–O(2′) • • • H–O(3) • • • H–O(2).

Conclusions.—Analysis of the isotope effects on hydroxy signals of glucose monomers and α-1→4 dimers is consistent with conclusions based on neutron scattering measurements on carbohydrates[21–23] and *ab initio* quantum mechanical calculations on model compounds[24] that hydroxy groups for which the oxygen atom accepts a hydrogen bond will tend to occur more frequently and to form stronger hydrogen bonds than those where the oxygen atom is a hydrogen-bond donor only. For molecules in Me_2SO solution hydroxy groups are largely involved in inter-molecular hydrogen bonding with the solvent and the intra-molecular hydrogen-bond chain length depends on the number of hydroxy groups in the molecule. The present observations of co-operative hydrogen-bond formation in carbohydrates provides evidence that such interactions may contribute to the stabilisation of particular hydrogen-bonding conformations in solution. Extrapolation of this behaviour to polymers such as amylose predicts that the hydrogen-bond network should form a continuous chain, that the process should be highly co-operative, and might be important in stabilising the helical conformation of the molecule. Evidence for weakly co-operative hydrogen bonding along the chain has previously been suggested from analysis of optical rotations of amylose in aqueous and dimethyl sulphoxide solutions.[25]

The SIMPLE n.m.r. method provides experimental evidence for a wide range of hydrogen bonds, from the relatively strong inter-residue hydrogen bond in maltose to the weaker intra-residue hydrogen bonds in the same molecule and glucose. However an important feature of the SIMPLE n.m.r. method of analysis is that measurements of very weak intramolecular hydrogen bonding of hydroxy groups can be made even though they may be participating in relatively strong intermolecular (*e.g.* solvent) hydrogen bonding at the same time.

Acknowledgements

We thank the S.E.R.C. for a postdoctoral research assistantship (to J. C. C.) and the M.R.C. for access to the 500 MHz n.m.r. spectrometer (N.I.M.R., London) and provision of n.m.r. computing facilities (Birkbeck College).

References

1 B. Casu, M. Reggiani, G. Gallo, and A. Vigerani, *Tetrahedron*, 1966, **22**, 3061; 1968, **24**, 803.
2 M. St-Jacques, P. R. Sundarajan, K. J. Taylor, and R. H. Marchessault, *J. Am. Chem. Soc.*, 1976, **98**, 4386.
3 J. C. Christofides and D. B. Davies, *J. Chem. Soc., Chem. Commun.*, 1982, 560.
4 J. C. Christofides and D. B. Davies, *J. Am. Chem. Soc.*, 1983, **105**, 5099.
5 E. Alvarado, O. Hindsgaul, R. U. Lemieux, K. Bock, and H. Pedersen, Abstract No. D720, p. 480 Abstracts of the XIIth International Carbohydrate Symposium, Utrecht, 1984.
6 J. C. Christofides and D. B. Davies, *J. Chem. Soc., Chem. Commun.*, 1985, 1533.
7 J. C. Christofides and D. B. Davies, *Magn. Reson. Chem.*, 1985, **23**, 582.
8 R. U. Lemieux and K. Bock, *Jpn. J. Antibiot.*, 1979, XXXII Suppl. S-163, 560.
9 B. Gillet, D. Nicole, J.-J. Delpuech, and B. Gross, *Org. Magn. Reson.*, 1981, **17**, 28.
10 A. Neuman, H. Gillier-Pandraud, and F. Longchambon, *Acta Crystallogr.*, 1975, **B31**, 474.
11 R. D. R. Gilardi and J. L. Flippen, *Acta Crystallogr.*, 1974, **B30**, 2921.
12 D. C. Rohrer, *Acta Crystallogr.*, 1972, **B28**, 425.
13 R. H. Marchessault and S. Perez, *Biopolymers*, 1979, **18**, 2369.
14 A. Matsumoto and M. Takasuka, *Carbohydr. Res.*, 1985, **137**, 13.
15 J. C. Christofides, D. B. Davies, J. A. Martin, and E. B. Rathbone, *J. Am. Chem. Soc.*, 1986, **108**, 5738.
16 R. R. Fraser, M. Kaufman, P. Morand, and G. Govil, *Can. J. Chem.*, 1969, **47**, 403.
17 A. J. Michell and H. G. Higgins, *Tetrahedron*, 1965, **21**, 1109.
18 G. A. Jeffrey and L. Lewis, *Carbohydr. Res.*, 1978, **60**, 179.
19 Y.-C. Tse and M. D. Newton, *J. Am. Chem. Soc.*, 1977, **99**, 611.
20 R. U. Lemieux and A. A. Pavia, *Can. J. Chem.*, 1969, **47**, 4441.
21 G. A. Jeffrey and S. Takagi, *Acc. Chem. Res.*, 1978, **11**, 264.
22 G. A. Jeffrey and J. Mitra, *Acta Crystallogr.*, 1983, **B39**, 469.
23 G. A. Jeffrey, M. E. Gress, and S. Takagi, *J. Am. Chem. Soc.*, 1977, **99**, 609.
24 M. D. Newton, *Acta Crystallogr.*, 1983, **B39**, 104.
25 D. A. Rees, *J. Chem. Soc. B*, 1970, 877.

Received 25th March 1986; *Paper* 6/593