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HYDROXYL-PROTON RESONANCE SHIFTS FOR A RANGE OF AQUEOUS SUGAR SOLUTIONS

M. C. R. Symons, J. A. Benbow, and J. M. Harvey
Department of Chemistry, Leicester University, Leicester LE1 7RH (Great Britain)

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ABSTRACT

At low temperature and in a narrow pH-range, the hydroxyl-proton resonance spectra of a range of mono-, di-, and oligo-saccharides in dilute aqueous solutions have been resolved. The signals rapidly broaden on raising the temperature and on changing the pH of the solutions. Optimum conditions for obtaining maximum resolution are described, and attempts are made to assign the resonances to specific hydroxyl groups. In all cases, the resonances for the anomeric hydroxyl-proton occurred at lowest field, and the pH value for optimum resolution of these resonances was always lower than that for the other hydroxyl resonances.

INTRODUCTION

When p.m.r. spectra of aqueous solutions of sugars are reported, they only contain features from C-H protons. This is because exchange between the O-H protons and water protons is rapid under the conditions employed. We have recently established that, under carefully controlled conditions, relatively narrow signals for hydroxyl protons can be detected[1,2]. A wide range of sugars has now been studied, and optimum conditions for obtaining resolved resonances have been defined.

EXPERIMENTAL

Sugars were of the highest grades available and were used as supplied; further purification had no effect on the n.m.r. spectra. Aqueous solutions of sugars were generally ~1.4M, and their pH values were measured at room temperature or at 0° with a Pye Dynacap HO5E°2 meter modified to take $E_0$7 electrodes. The pH values were controlled by a range of buffers at various concentrations, and optimum conditions were sought to give the narrowest signals. N.m.r. spectra were recorded on a Jeol PS-100 spectrometer over a range of temperatures (measured with a Comark thermocouple). In all cases, the possible interference of spinning side-bands from the strong peak for water was checked by altering the rate of sample spinning.

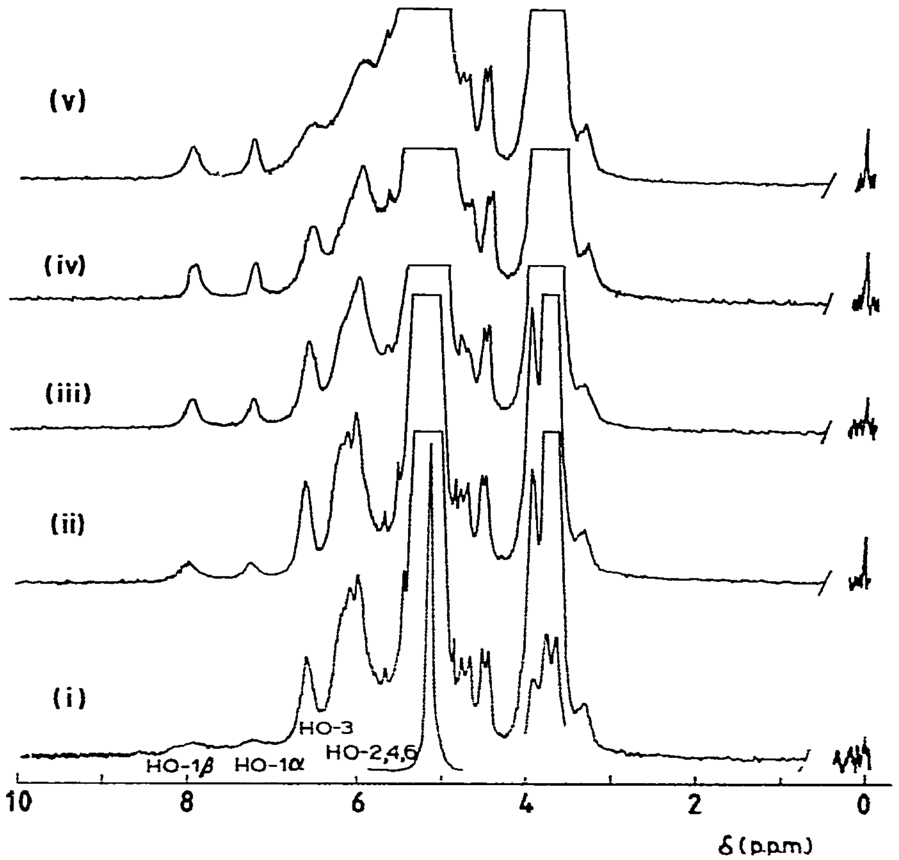

Fig. 1. N.m.r. spectra for lactose (1.15M) as a function of pH (buffer: mM NaH malate — mM maleic acid): pH values (i) 6.9, (ii) 6.6, (iii) 6.2, (iv) 5.7, and (v) 5.35. TSP reference is present at $\sim$1.2mM.

RESULTS

Some typical spectra are shown in Fig. 1 and the results are summarised in Tables I–III. The data in Table I record the effect of increasing the concentration of various buffers on the line-widths ($\Delta\nu_{1/2}$) of the resonances for the anomeric hydroxyl-proton and the resonance for water. The pH was adjusted to give minimum line-widths in each case (see Fig. 2 for some selected cases). In Tables IB and IC, data for a given buffer system (sodium hydrogenmalate + maleic acid) are given at various concentrations. The results show that the pH minima of the type shown in Fig. 1 shift with increasing concentration of buffer and that the minimum width increases. From these and other data, we decided that reproducible spectra were best obtained by using the malate–maleic acid buffer system at a concentration of $\sim$mM for each component. All further studies were carried out with this buffer.

Shifts (δ) from TSP [sodium 3-(trimethylsilyl)propionate: note that there

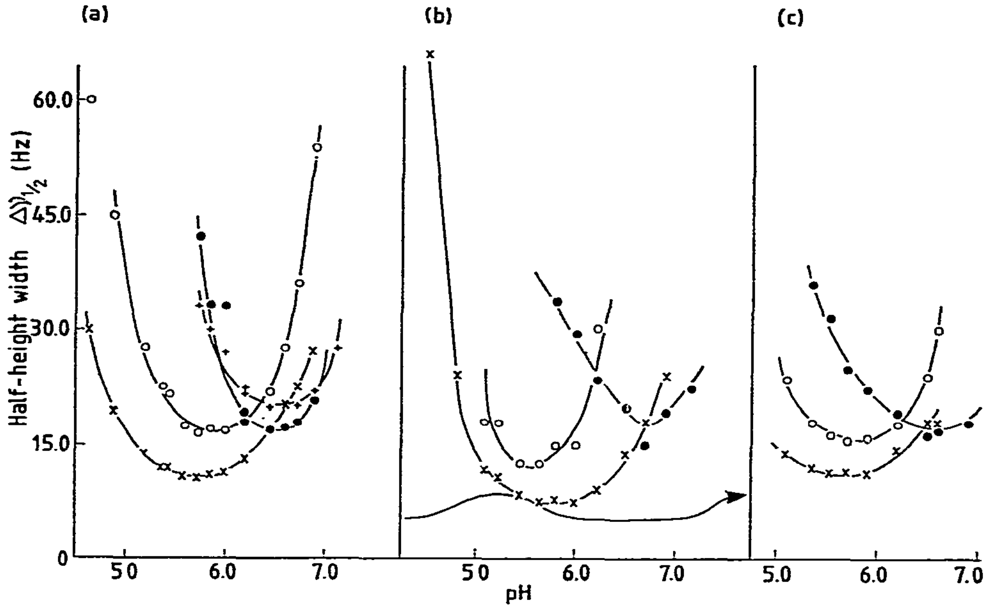

Fig. 2. Plots of pH *vs* half-height width for (*a*) D-galactose, (*b*) D-fructose, and (*c*) lactose. The symbols × and ○ refer to the α- and β-anomeric hydroxyl-groups, respectively, except for D-fructose where they represent the β-pyranose and β-furanose forms, respectively. The symbols ● and + refer to non-anomeric hydroxyl-groups. The unbroken trace in (*b*) shows how the half-height width of the water resonance varies with pH over the range indicated.

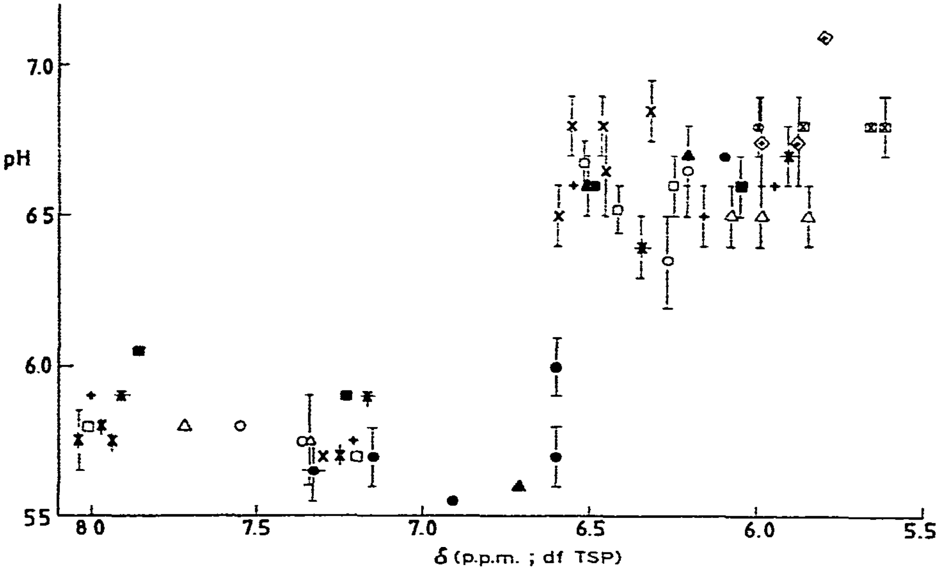

Fig. 3. A plot of chemical shift *vs* pH (for minimum line-widths): × D-glucose, + D-galactose, ○ D-mannose, □ D-xylose, △ D-ribose, ● D-fructose, ▲ L-sorbose, ■ D-fucose, ✳ 2-deoxy-D-*arabino*-hexose, ✱ lactose, -●- maltose, ⊕ D-glucitol, and ⊠ D-mannitol. Where the uncertainty in pH is greater than ±0.05 unit, this has been indicated.

TABLE I

EFFECTS OF VARIATION IN BUFFER CONCENTRATION ON THE LINE-WIDTHS FOR THE ^{1}H (HO-1) RESONANCES OF AQUEOUS α- AND β-D-GLUCOSE (1.5M)

A. For a range of buffers at pH values giving minimum widths

Buffer	*Conc. (mM)*	*β Anomer*			*α Anomer*			*Water*		
		$\Delta\nu_{1/2}$ *(Hz)*[a]	δ *(p.p.m.)*[b]	*pH*[c]	$\Delta\nu_{1/2}$ *(Hz)*[a]	δ *(p.p.m.)*[b]	*pH*[c]	$\Delta\nu_{1/2}$ *(Hz)*[a]	δ *(p.p.m.)*[b]	*pH*[c]
Sodium acetate	10	15	4.1	5.7	12	3.33	5.1~5.7	6.0	1.32	5.7~6.65
	100	broad	—	—	21.6	3.33	6.35	7.2	1.31	6.35~7.0
Sodium hydrogenmalate	10	18	4.1	5.5	12	3.35	5.7	5.7	1.33	5.9~6.6
	50	29.7	4.1	6.35	17.7	3.36	6.05	6.9	1.33	6.3~7.0
Maleic acid	10	17.7	4.1	5.85	11.4	3.35	5.85	6.0	1.34	6.0~7.0
	20	21	4.14	6.2	13.5	3.38	6.2	6.0	1.36	6.2~7.1
	50	28.5	4.1	5.8~6.1	17.7	3.35	6.1	6.9	1.33	6.6~6.9

[a]Measured at −9 ±1°. [b]Downfield shift from the most intense feature in the alkyl region of the ^{1}H-spectrum of D-glucose. [c]Measured at 0°.

B[a]. *For equimolar maleic acid/sodium hydrogenmalate buffer at pH 6.15*[b]

Buffer conc. (mM)[c]	*Temp. (degrees)*	*β Anomer*		*α Anomer*		*Water*	
		$\Delta\nu_{1/2}$ *(Hz)*	δ *(p.p.m.)*[d]	$\Delta\nu_{1/2}$ *(Hz)*	δ *(p.p.m.)*	$\Delta\nu_{1/2}$ *(Hz)*	δ *(p.p.m.)*
1	−9	16.8	4.14	13.2	3.4	6.6	1.37
10	−9	19.8	4.14	14.1	3.4	6.6	1.38
50	−9	35.1	4.14	20.4	3.4	9.0	1.38
1	+0.5	30.0	4.02	20.4	3.3	6.9	1.24
10	+0.5	32.4	4.02	22.8	3.29	7.5	1.23
50	+0.5	60.0	3.96	30.0	3.3	7.5	1.27

[a]Glucose concentration, 1.23M. [b]Measured at room temperature (~ +19°). [c]In each buffer. [d]As for *b* in Table IA.

C[a]. *For equimolar maleic acid/sodium hydrogenmalate buffer at pH 6.9*[b]

Buffer conc. (mM)[c]	*Temp. (degrees)*	*β Anomer*		*α Anomer*		*α,β Non-anomeric hydroxyl groups*[e]			*Water*	
		$\Delta\nu_{1/2}$ *(Hz)*	*δ (p.p.m.)*[d]	$\Delta\nu_{1/2}$ *(Hz)*	*δ (p.p.m.)*[d]	$\Delta\nu_{1/2}$ *(Hz)*	*δ (p.p.m.)*[d]	*δ (p.p.m.)*[d]	$\Delta\nu_{1/2}$ *(Hz)*	*δ (p.p.m.)*[d]
1	−9	33.0	4.1	23.4	3.38	42	2.6	2.11	5.4	1.37
10	−9	43.8	4.1	28.8	3.37	44	2.6	2.08	7.5	1.35
50	−9	40.8	4.12	24	3.4	46	2.58	broad	7.5	1.34
1	+0.5	—	—	—	—	54	2.4	—	7.8	1.24
10	+0.5	—	—	—	—	59	2.42	—	8.4	1.25
50	+0.5	—	—	—	—	87	~2.3	—	9.6	1.24

[a]Glucose concentration, 1.23M. [b]Measured at room temperature (~ +19°). [c]In each buffer. [d]As for *b* in Table IA. [e]The high-field resonance is HO-6 and the low-field value refers to the composite HO-2,3,4.

TABLE II

^{1}H-N.M.R. DATA FOR HYDROXYL PROTONS OF MONOSACCHARIDES IN WATER[a] AT −9 ±1°

Sugar (conc.)	Anomer[b]	Composition (%)[c]	Conformation[d]	Anomeric			Non-anomeric				Water		
				$\Delta\nu_{1/2}$[e]	δ[f]	pH[g]	$\Delta\nu_{1/2}$[e]	δ[f]	pH[g]	Assignment	$\Delta\nu_{1/2}$[e]	δ[f]	pH[g]
D-Glucitol	Acyclic						sh	5.96	6.6~6.9		5.2	5.29	6.4~7.4
(1.39M)							sh	5.80	6.6~6.9				
							30	5.89	7.1				
D-Mannitol	Acyclic						19	5.86	6.8		5.2	5.16	<6.6~7.1
(1.26M)							16	5.66	6.8				
							sh	5.62	~6.8				
D-Glucose	βp	56.5	$^4C_1$; eq.	15.6	8.04	5.75	sh	6.56	~6.8	HO-3,4	7.5	5.25	6.0~7.1
(1.23M)	αp	43.5	$^4C_1$; ax.	10.5	7.30	5.7	~24	6.47	~6.8				
							sh	6.32	~6.85	HO-2			
							~24	6.00	~6.8	HO-6			
(1.10M)[h]	αp		$^4C_1$; ax.	11.5	7.28	5.7	sh	6.59	~6.5 w	HO-3,4	5.4	5.25	6.0~7.1
							17	6.46	6.5~6.8				
							sh	6.35	~6.8	HO-2			
							~18	6.00	6.8~6.9	HO-6			
D-Galactose[i]	βp	60	$^4C_1$; eq.	16.5	8.0	5.9	17	6.55	6.6	HO-3	8.4	5.28	6.1~7.0
(1.38M)	αp	40	$^4C_1$; ax.	10.5	7.21	5.75	sh	6.16	~6.5	HO-2,6,4			
							20	5.95	6.6				
D-Mannose	βp	~30	$^4C_1$; eq.	15.0	7.55	5.8	31[j] sh	6.27	6.2~6.5	HO-2,3,4	5.4	5.24	5.9~7.0
(1.25M)							s	6.21	6.5~6.8				
	αp	~70	$^4C_1$; ax.	12.3	7.36	5.75	~30	6.00	~6.8	HO-6			

D-Xylose	βp	58	$^4C_1$; eq.	17.4	8.01	5.8	~24	6.52	6.6~6.75	HO-3,4	5.4	5.18	5.7~7.0
(1.45M)	αp	42	$^4C_1$; ax.	12.6	7.20	5.7	~18	6.42	6.45~6.6				
							sh	6.25	~6.6	HO-2			
D-Ribose[k]	βp	βp > αp	$^4C_1 \leftrightarrows {}^1C_4$	15.0	7.72	5.8	31[j] sh	6.08	6.4~6.6	HO-2,3,4	5.4	5.16	5.6~6.7
(1.42M)			$^4C_1 \leftrightarrows {}^1C_4$	< 15.0	7.34	5.6~5.9	sh s	5.99	6.4~6.6				
	αp							5.85	6.4~6.6	[i]			
D-Fructose[l,m]	βp	~78	$^2C_5$; ax.	7.5	6.60	~5.7[i,j]	7.5	6.60	~6.0	[i,j]	5.4	5.29	6.2~7.1
(1.41M)	βf	~14	—	12.0	6.91	5.55	16.5	6.10	6.7	HO-1,3,4,5			
	αf	~3	—	12.0	7.15	5.6~5.8							
L-Sorbose[m]	αp	—	$^2C_5$; ax.	9.0	6.71	5.6	15	6.51	~6.6	HO-4,5	5.1	5.30	5.9~7.0
(1.31M)							21	6.21	~6.7	HO-1,3			
D-Fucose	βp	63	$^4C_1$; eq.	15.0	7.86	6.05	12.6	6.49	6.6	HO-3	5.1	5.26	5.8~7.0
(1.06M)	αp	37	$^4C_1$; ax.	9.6	7.23	5.9	21[j] sh	6.05	~6.6	HO-2,4			
							18	6.05	~6.6	HO-2,4			
2-Deoxy-D-	βp	44	$^4C_1$; eq.	16.5	7.91	5.9	25[j] sh	6.35	~6.4	HO-3,4	5.1	5.24	5.8~7.1
arabino-hexose							21						
(1.4M)	αp	56	$^4C_1$; ax.	10.8	7.17	5.9	27	5.91	~6.7	HO-6			

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[a] Solutions were buffered with mM NaH malate and mM maleic acid in doubly glass-distilled water (deionised). Mannitol was measured at −4 ±1°. [b] βp and αp refer to the β and α anomers of the pyranose forms; βf refers to the β-furanose form. [c] Determined by integration, and the average of several runs (error, ~ ±5%). [d] The inserts "ax." (= axial) and "eq." (= equatorial) refer to the position of the anomeric hydroxyl group with respect to the plane of the ring. [e] Reported in Hz: sh, shoulder. [f] Reported in p.p.m. downfield of added TSP (~ mM). [g] pH Value [measured at room temperature (~22°)] required for minimum line-width: "~" indicates uncertainty of ~ ±0.1 pH-unit. [h] The pH was measured at 0°, and the solutions contain preponderantly the αp species: w, weak signal from βp species. [i] Weak signals: probably from furanose hydroxyl-protons. [j] A composite peak: sh, shoulder; s, appearance of a single, broad resonance. [k] The furanose anomeric-hydroxyl resonances were also observed: βf (~7.52 p.p.m.) and αf (~ −7.02 p.p.m.). [l] Tentative assignment of pyranose resonances. [m] Weak, spurious peaks or shoulders were also observed; for fructose, these occurred at δ 7.29, 7.01, and 6.79 (could be αp present in < 5%); for sorbose, these occurred to low field of the anomeric signals.

TABLE III

^{1}H-N.M.R. DATA FOR HYDROXYL PROTONS OF DI- AND OLIGO-SACCHARIDES IN WATER[a] AT $-9 \pm 1°$

Sugar (conc.)	*Residues*	*Anomer*[b]	*Composition (%)*[c]	*Anomeric*			*Non-anomeric*				*Water*		
				$\Delta\nu_{1/2}$[e]	δ[f]	*pH*[g]	$\Delta\nu_{1/2}$[e]	δ[f]	*pH*[g]	*Assignment*	$\Delta\nu_{1/2}$[e]	δ[f]	*pH*[g]
Lactose	*β*-D-Gal*p*-(1→4)-	*βp*	53	15.6	7.97	5.8	16	6.60	6.6	HO-3 (Glc)	5.4	5.19	5.7~6.9
(1.15M)	*α,β*-D-Glc*p*	*αp*	47	11.4	7.25	5.7				HO-3 (Gal)			
							33[j] sh	6.19	6.5~6.6	HO-2 (Glc)			
							s	6.11	6.6~6.9	HO-2,6,4 (Gal)			
							18	6.01	~6.7	HO-6 (Glc)			
(1.40M)[n]		*βp*	52	15.0	7.94	5.75	15.6	6.57	6.6		5.7	5.18	5.7~6.9
		αp	48	11.4	7.20	5.7	33[j] sh	6.16	6.7~6.9	As above			
							s	6.10	6.6~6.7				
							18	5.98	6.6~6.7				
Maltose	*α*-D-Glc*p*-(1→4)-	*βp*	53	22.0	8.04	~5.75	sh	6.64	6.4~6.6	HO-4	6.5	5.24	5.8~7.0
(1.18M)	*α,β*-D-Glc*p*	*αp*	47	13.0	7.33	~5.65	24	6.48	6.4	HO-3			
							sh	6.45	~6.4	HO-2			
							24	5.90	~6.8	HO-6			
Sucrose	*α*-D-Glc*p*-(1→2)-*β*-D-Fru*f*						16	6.79	6.3	HO-3 (Fru)[o]	6.0	5.23	5.7~7.1
(1.20M)							22	6.46	6.45	HO-4 (Fru)[o]			
										HO-3,4 (Glc)			
							sh	6.34	6.3~6.4	HO-2 (Glc)			
							sh	6.06	~6.4	HO-1 (Fru)			
							18	5.92	6.7	HO-6 (Glc)			
										HO-6 (Fru)			

Raffinose (0.51M)	α-D-Gal*p*-(1→6)-α-D-Glc*p*-(1→2)-β-D-Fru*f*	13	6.75	~6.3	HO-3 (Fru)[o]	5.1	5.19	5.7~6.9
		20	6.43	~6.6	HO-4 (Fru)[o]			
					HO-3 (Gal)			
					HO-2 (Glc)[l]			
		36[j] sh	6.10	6.3~6.6	HO-1 (Fru)			
		27	6.02	~6.6	HO-2,6,4 (Gal)			
					HO-3,4 (Glc)[l]			
					HO-6 (Fru)			
Melezitose (0.48M)	α-D-Glc*p*-(1→3)-β-D-Fru*f*-(2→1)-α-D-Glc*p*	11.4	6.99	6.2	HO-4 (Fru)[o]	4.5	5.26	5.8~6.8
		15.3	6.57	6.45	HO-3,4 (Glc)			
		sh	6.46	6.2~6.6	HO-2 (Glc)			
		18	6.11	6.4~6.5	HO-1 (Fru)[o]			
					HO-6 (Fru)			
		sh	6.02	6.5~6.7	HO-6 (Glc)			
Stachyose (0.24M)	α-D-Gal*p*-(1→6)-α-D-Gal*p*-(1→6)-α-D-Glc*p*-(1→2)-β-D-Fru*f*	14.4	6.73	6.4	HO-3 (Fru)[o]	5.7	5.15	5.8~7.0
		18.6	6.42	6.6	HO-4 (Fru)[o]			
					HO-3 (Gal)			
					HO-2 (Glc)			
		34[j] sh	6.06	6.3~6.6	HO-1 (Fru)			
		21	5.99	6.6~7.0	HO-3,4 (Glc)			
					HO-2,6,4 (Gal)			
					HO-6 (Fru)			
Cyclohexa-amylose (0.13M)	$\{$α-D-Glc*p*-(1→4)$\}_6$ cyclic	11.5	6.19	6.0	HO-2,3	5.1	4.84	5.1~6.7
		~12	5.97	~6.0				
		~13.5	5.92	~6.0				
		18.0	5.75	6.5~6.7	HO-6			
Cyclohepta-amylose (0.052M)	$\{$α-D-Glc*p*-(1→4)$\}_7$ cyclic	12.0	6.51	~6.2	HO-2,3	5.1	5.02	5.0~6.6
		~12	6.22	~6.2				
		~12	6.17	~6.2				
		sh	~5.84	>6.6	HO-6			

[a,b,c,e,f,g,j,l] See Table II. [n] Analytical Reagent Grade. [o] Tentative assignment of furanose resonances.

was no detectable shift between the C-H resonances for the sugars and the TSP resonance when the pH was changed] and half-widths ($\Delta\nu_{1/2}$) for this buffer system at —9° are given in Tables II and III. These shifts are displayed as a function of the pH minima in Fig. 3. (In the following discussion, D sugars are referred to unless stated otherwise.)

DISCUSSION

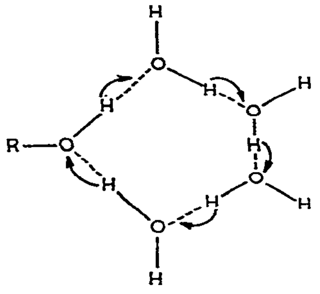
Our main aim was to discover optimum conditions for obtaining well-resolved hydroxyl-proton resonances for aqueous solutions of sugars. All of the mono-, di-, and oligo-saccharides examined have given well-defined and characteristic features, and it is clear that the procedure can be used as a significant analytical tool.

pH-Dependence. Curves of the type shown in Fig. 2 were obtained in all cases. The reactions responsible for the broadening are:

$$\mathrm{ROH} + \mathrm{OH}^- \rightleftharpoons \mathrm{RO}^- + \mathrm{H_2O} \quad \text{and} \tag{1}$$

$$\mathrm{ROH} + \mathrm{H_3O}^+ \rightleftharpoons \mathrm{ROH_2^+} + \mathrm{H_2O}. \tag{2}$$

It is possible that a pH-independent mechanism also operates, such as that depicted in **1**.



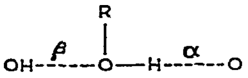
1

The shifts in pH minima, which are most marked for the anomeric hydroxyl-proton resonances, can be understood if a reciprocal change in the acidic and basic strengths of the hydroxyl groups is postulated. Thus, for the anomeric hydroxyl groups, the acidity is enhanced, and the basicity decreased. The $[\mathrm{OH}^-]$ needed to remove the proton is therefore diminished, but the $[\mathrm{H_3O}^+]$ needed to protonate significantly at oxygen is enhanced, so the pH-minima shift to low pH values.

The widths of the water resonance vary in the expected manner. When any one of the hydroxyl resonances is broad, this is reflected in an increase in width for the water peak. When they are all narrow, so is the water peak, and when they have been completely lost, in the fast-exchange region, the water peak again becomes narrow. This confirms Eqs. *1* and *2* and formula **1**, and the width-increments could be used to estimate the net rates of these processes.

Assignment of hydroxyl-proton resonances. Assignments are suggested in the Tables; these have not been verified in all cases, since precise assignment was not our prime concern. For all sugars containing anomeric hydroxyl-protons, the lowest-field resonances are assigned to these protons. For several sugars whose assignments in dimethyl sulphoxide solution were known, the trends in peak positions as a function of the concentration of water in mixed solvent systems were followed, and extrapolated to pure water. We accept that the protons of axial hydroxyl groups resonate at higher fields than their equatorial counterparts. Also, the presence of an axial hydroxyl group seems to cause an upfield shift for the resonances of neighbouring, equatorial hydroxyl groups. For example, the HO-2 resonance of galactose and the HO-3 and HO-4 resonances of mannose are to high-field of those for glucose and xylose. Similarly, for D-ribose, the non-anomeric hydroxyl resonances are shifted to high field because of the axial HO-2 and HO-4 groups in the $^1C_4$ conformation and the axial HO-3 group in the $^4C_1$ conformation. For D-fructose, the resonance at $\delta \sim 6.6$ appears to be a composite. Certainly the anomeric hydroxyl-protons contribute, but there may also be a contribution from non-anomeric hydroxyl-protons of the furanose form. Assignments for the oligosaccharides are based on those for their component monosaccharides.

Shifts. These are governed by at least three factors, namely (*a*) structural, (*b*) acidity, and (*c*) basicity. It is noteworthy that all of these resonances occur downfield of the water resonance, and this seems to be characteristic of all aqueous, alcoholic systems. Factors (*b*) and (*c*) work together, and tend to buffer each other. Both types of hydrogen bond normally formed by hydroxyl groups (**2**, α and β) contribute to the downfield shift. The β bond enhances the strength of the α bond, so an increase in oxygen basicity alone would increase the strength of the β hydrogen-bond and hence also the α bond, causing a downfield shift of the ROH proton. Generally, however, an increase in basicity is accompanied by a decrease in acidity, which will directly weaken the α bonds, causing an upfield shift. On balance, the acidity effect usually dominates. This explains the large shift to low fields for the anomeric protons. However, the trend in Fig. 3 is very poorly defined, and clearly other factors must play a part.



$$\mathrm{OH}\overset{\beta}{\cdots\cdots}\overset{\overset{\displaystyle\mathrm{R}}{|}}{\mathrm{O}}-\mathrm{H}\overset{\alpha}{\cdots\cdots}\mathrm{O}$$

2

In our view, the steric factor is important. Thus, for glucose and galactose in the pyranoid forms, HO-1α is axial, and solvation will be subject to greater constraints from the molecule than that for HO-1β which is equatorial. Similarly, the observation that protons of axial hydroxyl groups resonate at higher fields than their equatorial counterparts may arise because solvation by water is less hindered for the equatorial groups. Also, the effect, mentioned above, of an axial hydroxyl group on the resonances of neighbouring equatorial groups may again reflect an interference in their solvation (see Tables II and III). For β-D-fructose and α-L-sorbose, steric interference (by the CH_2OH group attached to C-2) with solvation probably causes an extra upfield shift of the resonances for the anomeric hydroxyl-protons. Similar explanations can be advanced for several of the results shown in Fig. 3. However, our main concern here is to establish that each sugar gives rise to a characteristic set of O-H resonances, and these are always narrow under our defined conditions, at least for the range of mono-, di-, and tri-saccharides that we have studied.

Spin-coupling. In general, the hydroxyl-proton resonances were so broad that the expected coupling to the C-H protons was not resolved. However, under optimum conditions, the proton resonances for certain anomeric hydroxyl groups were markedly flat-topped and hence estimates of the coupling constants could be obtained. For example, for glucose, $J_{1,HO\text{-}1}$ is ~4 and 7 Hz for the α and β anomers, respectively. These values are close to those (4.5 and 6.7 Hz) obtained from solutions in dimethyl sulphoxide.

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