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HYDROXYL PROTON RESONANCES OF SUGARS IN DIMETHYLSULPHOXIDE SOLUTION

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NMR spectroscopy has been recently used for conformational studies on carbohydrates[1,2,3,4]. Among the significant results in D_2O solution, the correlation of the chemical shift and the coupling constant of the C_1H proton to the configuration (α or β) of the anomeric center has been established[5,6]. However, the NMR spectrum of a reducing sugar in D_2O displays the signals of both anomers, owing to the mutarotation after dissolution. It appeared worthwhile to investigate NMR spectra of carbohydrates in a solvent in which mutarotation did not take place and dimethylsulphoxide (DMSO) was selected for this purpose. Recently Chapman and King[7] pointed out that alcohols in DMSO solution display well resolved peaks, which are also splitted by coupling whith the protons on the adjacent carbon atom. The chemical shifts of the OH protons were reported for a number of representative alcohols, among them β-arabopyranose, α-glucopyranose and α-fructopyranose, for which only the O_1H absorption is given.

DMSO is a good sugar solvent and, as stated above, it does not give mutarotation on most dissolved saccharides. The spectrum in DMSO therefore corresponds to the anomeric form of the solid sugar and NMR spectroscopy in DMSO solution appears to be the most direct method for detecting the anomeric configuration. Furthermore a mixture of anomers

TABLE I

Chemical shifts (τ values ppm) of the O_1H proton in DMSO and coupling constants (cps) J_{O_1H/C_1H}.

Carbohydrates	α-anomer (O_1H axial)		β-anomer (O_1H equatorial)	
	τ	J	τ	J
Glucose	3.85	4.5	3.48*	7.0*
Galactose	3.95	4.0	-	-
Ramnose	3.86	4.0	-	-
Xylose	3.90	4.5	3.50*	6.0*
2-deoxy-glucose	3.96*	4.0*	3.58	6.5
Cellobiose	3.72*	4.5*	3.42	7.0
Gentiobiose	3.84*	4.0*	3.50*	6.0*
Lactose	3.72*	4.5*	3.40	6.0*
Maltose	3.70*	4.5*	3.40	6.5
Melibiose	3.86*	4.0*	3.54*	6.0*

* data taken from the equilibrium mixture of the anomers.

All the spectra were measured on a Varian A-60 spectrometer, with reference to internal tetramethylsilane.

TABLE II

NMR spectrum of α-glucose

Chemical shifts τ (ppm)		Multiplicity	Coupling constant J (cps)		Assignment
3.85		doublet	4.5		O_1H
5.07		triplet	4.0		O_5H
5.30		doublet	7.0		
5.38		doublet	7.0		O_2H, O_3H, C_4H
5.60		doublet	6.5		
5.68	5.62	doublet	4.5	7.0	C_1H
	5.74	doublet	4.5		

can be conveniently analyzed in the actual amounts of the components.

In the range accessible with DMSO as solvent (up to 6 τ) the signals of all the hydroxyl protons are displayed together with the "anomeric" C_1H proton. The most downfield signal corresponds to the O_1H proton, which gives a well recognizable doublet in the 3,4 - 4,0 τ region. The chemical shifts of the O_1H signal and the O_1H/C_1H coupling constants are reported in Table I for a number of carbohydrates, having the reducing ring with the configuration of glucose at C_1 and C_2. α-anomers absorb between 3.70 and 3.96 τ and β-anomers between 3.40 and 3.58 τ , beeing the coupling constants of the order of 4.0 - 4.5 cps and of 6.0 - 7.0 cps respectively. Sugars with configuration at C_2 different from that of glucose (such as mannose and arabinose) show values which do not fit in the mentioned ranges, suggesting a possible influence of the C_2 configuration on the anomeric hydroxyl.

The resonances of the other hydroxyl protons can be generally observed in the range 4.9 - 6.0 τ, overlapping each other to some extent and superimposing the C_1H proton peak. As representative the spectra of α-glucose and α-methylglucoside are reported in figs. 1 and 2. The peaks of α-glucose have been attributed as shown in Table II. The two doublets at 5.62 and 5.74 τ have been assigned to the C_1H proton, assuming that it couples with the protons at O_1 and at C_2. In the spectrum of α-methylglucoside the doublet expected for the C_1H is partially hidden by the OH absorptions; it was then identified from the spectrum of the α-methylglucoside deuterated prior dissolution in DMSO (fig. 2).

The extent of overlapping of the hydroxyl peaks increases going from monosaccharides to polysaccharides and therefore well resolved spectra are usually observed only for the former ones. Anyhow some features of polysaccharide spectra are promising in distinguishing different types of glycosidic linkages. For instance, α-1,4 linked sugars show an absorption corresponding to two hydroxyl groups per disaccharide unit in the unusual range 4.0 - 4.8 τ (α-1,6 linked sugars absorb, as expected, at fields higher than 4.9 τ), suggesting a

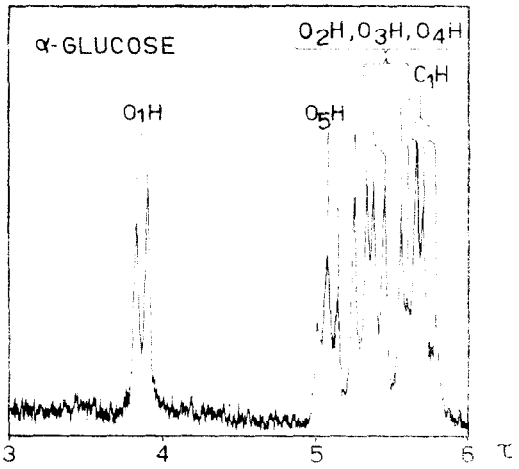

Fig. 1. NMR spectrum of α-glucose in DMSO.

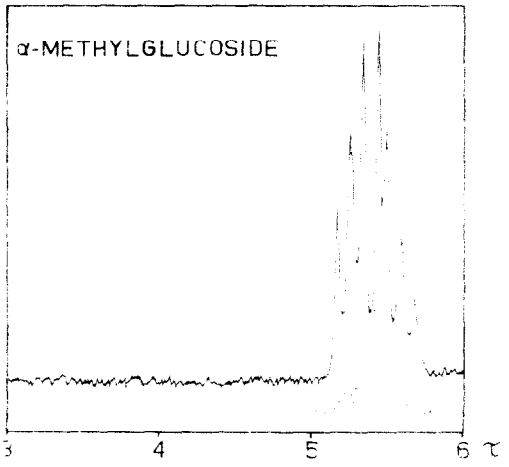

Fig. 2. NMR spectrum of α-methyl-glucoside in DMSO.
Dotted line refers to the deuterated product.

different interaction among the hydroxyl protons and the solvent. Further studies are in progress to correlate the extent of interaction between the hydroxyls and the solvent molecules, as obtained from NMR data, to the conformation of sugars.

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REFERENCES

(1) R.U.Lemieux, R.K.Kullnig, H.J.Bernstein and W.G.Schneider, J. Am. Chem. Soc., 80, 6098 (1958).

(2) R.W.Lenz and J.P.Heeschen, J. Polymer Sci., 51, 247 (1961).

(3) V.S.R.Rao, J.F.Foster and R.L.Whistler, J. Org. Chem., 28, 1730 (1963).

(4) L.D.Hall, Tetrahedron Letters, 1457 (1964).

(5) J.M. van der Veen, J. Org. Chem., 28, 564 (1963).

(6) V.S.R.Rao and J.F.Foster, J. Phys. Chem., 67, 951 (1963).

(7) O.L.Chapman and R.W.King, J. Am. Chem. Soc., 86, 1256 (1964).