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Preliminary Communication

Longitudinal relaxation-times of the anomeric protons of oligosaccharides

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As part of a continuing programme[1] to evaluate the potential of longitudinal nuclear relaxation-times (T_1-values) as probes for structural assignments of carbohydrate derivatives, we now report the first proton T_1-values for oligosaccharide derivatives.

These data, summarized in Table I, show clearly several interesting dependencies. First, it is noteworthy that, for the reducing end-group, the axially oriented proton always has a shorter relaxation-time than its equatorially oriented counter-

TABLE I

VALUES OF THE LONGITUDINAL RELAXATION-TIMES[a] (T_1-VALUES, SEC) FOR THE ANOMERIC PROTONS OF VARIOUS OLIGOSACCHARIDES[b]

Compound	*Reducing end*			*Non-reducing end*			*Acetone*
	H-1α	*H-1β*	*Ratio* $\frac{\alpha}{\beta}$	*H-1α*	*H-1β*	*Ratio* $\frac{\text{reducing}}{\text{non-reducing}}$	
D-Glucose[c]	4.2	2.3	1.9				
Maltose	2.5	1.1	2.2	0.86		2.9	16.3
Cellobiose	2.1	1.1	1.9		0.52	2.1	17.2
Lactose	2.1	1.1	1.8		0.54	2.1	16.9
Melibiose	2.6	1.3	1.9	1.1		2.3	16.1
Gentiobiose	2.3	1.2	1.9		0.59	2.0	15.9
Gentiobiose[d]	4.7	2.5	1.9		1.4	1.7	23.9
Sucrose				1.1			16.6

[a]Measured with a Varian XL-100 (15) spectrometer equipped with a Varian 620L (16K) computer, and using a 3-pulse (180°−90°−90°) sequence supplied by Varian Associates. [b]Unless otherwise stated, 5% solutions in 99.96% D_2O were used. The solutions were lyophilised once with deuterium oxide and then degassed by six freeze–pump–thaw cycles. Measurements were made at probe temperature (42°). A small amount of acetone was added as an internal reference. [c]10% solution. [d]3.3% solution at 65°.

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part; this behaviour is similar to that shown by monosaccharides[2]. However, in contrast to the monosaccharides, additional, wide variations are observed between the numerical values for the individual sugars; these variations are parallel to those exhibited by a small amount of acetone added as an internal reference. Although the source of these variations is not yet proven, it is quite clear that the viscosity of the solution is important; thus the T_1-values increase with increase in temperature and with decrease in concentration of the sugar. Fortunately, regardless of the individual numerical values, the ratio of the relaxation times of the H-1α and H-1β resonances appears to be constant for each particular sugar; this ratio is $\sim$1.9, except for maltose.

The second point of interest is that the anomeric-proton resonance for the non-reducing end group also shows a configurational dependence (compare maltose and cellobiose). Furthermore, the fact that the T_1-values of these protons are so much shorter than those of H-1 at the reducing end provides a potentially useful basis for assigning the individual resonances of the anomeric protons of oligosaccharides.

Finally, it is noteworthy that all of these anomeric-proton relaxation-times are very much shorter than that of water. It is thus a trivial matter[3] to use a Fourier Transform method to remove the residual, HOD peak from the n.m.r. spectrum of a polysaccharide. The delay time between the 180° and the 90°-pulse is selected such

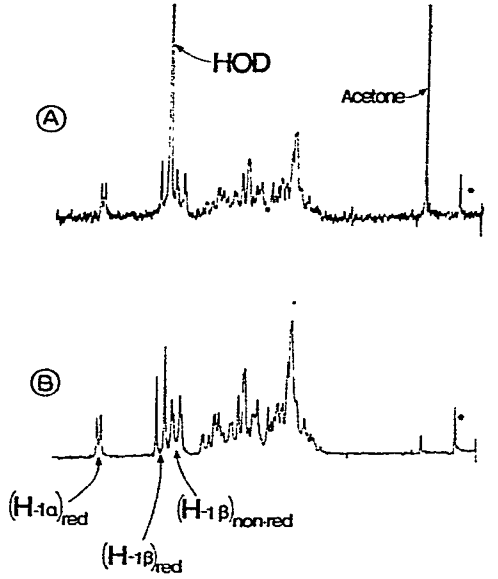

Fig. 1. Proton magnetic resonance spectra of a 5% solution of gentiobiose in deuterium oxide (99.96%); the sample had previously been lyophilised once with deuterium oxide and then degassed by six freeze–pump–thaw cycles. [A], the normal Fourier Transform spectrum (one scan); [B], is the water-nulled spectrum (10 scans). In this mode of operation the magnetisation is inverted by a 180° pulse and this is followed, after a delay time of 0.7 times the T_1-value of water, by a 90°-pulse. A spurious peak is indicated by an asterisk.

that the magnetisation of the slowly relaxing, HOD nuclei has effectively decayed to zero intensity at the time when the monitoring 90°-pulse is applied; this period is sufficient for the more-rapidly relaxing sugar protons to have recovered their equilibrium magnetisation and hence give signals in the n.m.r. spectrum. This is illustrated in Fig. 1. We have found this to be an invaluable aid in studies of sugars in aqueous solutions.

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