A Configuration Dependence of the Longitudinal Relaxation Times of Carbohydrate Derivatives

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Summary A Fourier Transform method has been used to measure the longitudinal relaxation times of the anomeric protons of eight anomeric pairs of pyranose derivatives; in every instance the axial proton has a shorter relaxation time than its equatorial counterpart.

WITH the advent[1,2] of highly selective techniques for the determination of nuclear relaxation times, it is now possible to investigate the diagnostic potential of this class of n.m.r. parameters. We now report a configuration dependence of the longitudinal relaxation times (T_1-values) of the anomeric protons of pyranose carbohydrates. The data listed in the Table were obtained *via* a F.T. method, using solutions that had been degassed by repeated freeze–pump–thaw cycles. With the exception of the two D-mannose derivatives (**3**) and (**5**), the assignments of the anomeric protons were trivial.

From the data listed for D-glucose (**1**), D-galactose (**2**), and 2-acetamido-2-deoxy-D-glucose (**4**) it is evident that an axially oriented proton has a shorter T_1-relaxation time than its equatorially disposed counterpart. It is tempting to ascribe this differential to the different degrees of dipole–dipole relaxation that H_{1a} and H_{1e} have with H_{3a} and H_{5a} by virtue of their different spatial separations. That the T_1 differential exists with substituents other than hydroxy at C_1, is clearly demonstrated by the data given for α and β methyl D-glucopyranoside (**6**) and α and β methyl D-xylopyranoside (**7**); the latter data show that the dependence also applies for pentopyranoses. It is also obvious from the data for the pair of 1,2,3,4,6-penta-*O*-acetyl-D-glucopyranoses (**8**), that esterification of the other hydroxy substituents leaves the T_1-differential essentially unchanged, although the absolute values of T_1 are reduced by *ca.* 40%.

TABLE. *Longitudinal relaxation times*[a] (*T_1-values, in sec*) *for the anomeric protons of pyranose carbohydrates*[b]

Compound		H_1 (Axial)	H_1 (Equatorial)
D-Glucose (**1**)[c,d]	α		6·4
	β	3·4	
D-Galactose (**2**)[c,e] ..	α		7·0
	β	3·9	
D-Mannose (**3**)[c]	α		6·3
	β	1·8	
2-Acetamido-2-deoxy-D-glucopyranose (**4**)[c,d] ..	α		4·7
	β	2·3	
2-Acetamido-2-deoxy-D-mannopyranose (**5**)[c]	α		4·9
	β	1·1	
Methyl D-glucopyranoside (**6**)[c,f]	α		2·4
	β	1·6	
Methyl D-xylopyranoside (**7**)[c,g]	α		3·8
	β	2·2	
1,2,3,4,6-penta-*O*-acetyl-D-glucopyranose (**8**)[h] ..	α		3·7
	β	2·0	

[a] Measured with a Varian XL-100 instrument fitted with a Varian 620L computer programmed for a 16K F.T., at a probe temperature of *ca.* 42° unless otherwise stated. [b] *Ca.* 10% w/v. [c] In 99·96% deuterium oxide. [d] Sample temperature, 46°. [e] Sample temperature, 49°. [f] T_1 for OMe: $\alpha = 2{\cdot}5$, $\beta = 3{\cdot}1$ s. [g] T_1 for OMe: $\alpha = 2{\cdot}6$, $\beta = 2{\cdot}7$ s. [h] In deuteriobenzene.

If this differential is general, and there seems to be no reason why it should not be, then it provides the basis of a new method for assigning configuration, which might be applicable when other n.m.r. methods are ambiguous. For example, distinction between the two anomeric proton resonances of D-mannose (**3**) and 2-acetamido-2-deoxy-D-mannopyranose (**5**) cannot be made on the basis of their coupling with H_2. Yet a sizable differential exists in their T_1 values that, in light of the other data discussed above, leads one to assign the lower field doublet to the α-anomer in both instances. An additional dependence, partially exemplified by derivatives (**1**, **3**) and (**4**, **5**) involves vicinally related protons; their interaction is larger when they have a *gauche* orientation.

It also seems probable that substituents other than the protons directly attached to the ring carbon atoms will show a configurational dependence of their T_1-values, although the differential is likely to be smaller in magnitude. This is so for the methoxy resonances of (**6**) and (**7**).

(*Received*, 24*th October* 1972; *Com.* 1809.)

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