

# INTERPRETATION OF $^{13}\text{C}$ SPIN-LATTICE RELAXATION TIMES IN OLIGOSACCHARIDES BY MEANS OF A BISTABLE JUMP MODEL

A. Ejchart,<sup>a</sup> T. Kozar,<sup>b</sup> N.E. Nifant'ev,<sup>c</sup> H. Grosskurth<sup>d</sup> and J. Dabrowski<sup>d</sup>

<sup>a</sup> Universität Bayreuth, LS Biopolymere, Bayreuth, Germany,

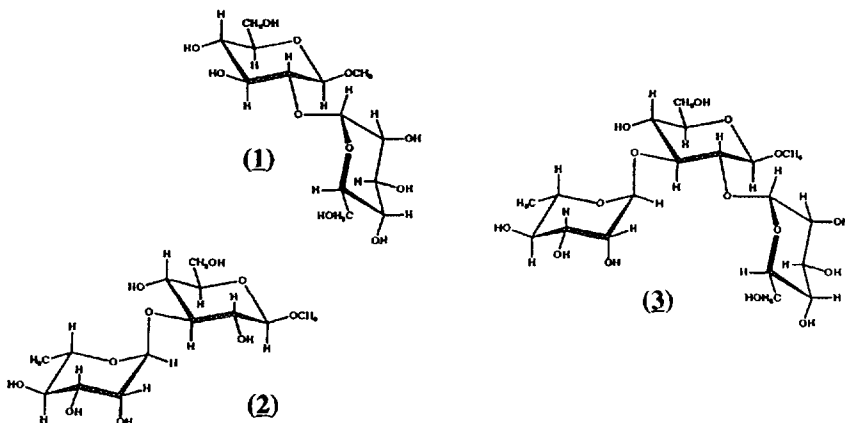
<sup>b</sup> Institute of Experimental Physics, Department of Biophysics, Košice, Slovakia,

<sup>c</sup> Zelinsky Institute of Organic Chemistry, Moscow, Russia,

<sup>d</sup> Max-Planck-Institute für Medizinische Forschung, Heidelberg, Germany.

## INTRODUCTION

Nuclear relaxation is an important source of information on the dynamics of molecules in solution. While seeking for new experimental proof of the conformational mobility about glycosidic bonds in fucosylated lactoses, we found that the  $^{13}\text{C}$  spin-lattice relaxation times measured at two different magnetic fields reflected both the anisotropic overall tumbling of the molecules, and internal jumps of the fucose residues about the glycosidic bonds [1]. The quantitative interpretation of the  $T_1$  values requires, however, the use of an appropriate model of the molecular motion and corresponding spectral densities.



$T_1(^{13}\text{C})$  relaxation times for D-Man $\alpha$ (1→2)-D-Glc $\beta$ 1-OMe (1), L-Rha $\alpha$ (1→3)-D-Glc $\beta$ 1-OMe (2) and D-Man $\alpha$ (1→2)[1.-Rha $\alpha$ (1→3)]-D-Glc $\beta$ 1-OMe (3) were measured at four different magnetic fields [2]. Interpretation of these data in terms of spectral densities derived for axially symmetric or fully anisotropic tumbling of rigid molecule [3] has partially failed, thus giving a strong support to the expected conformational flexibility of these oligosaccharides, as found with use of  $^1\text{H}$  NOE measurements and Molecular Mechanics calculations. Recently we applied a bistable jump model for segmental motion with modulation of internuclear distances [4] in order to remove deviations observed when molecular rigidity was assumed.

## RESULTS AND DISCUSSION

**Table 1.** Overall rotational diffusion constants ( $s^{-1}$ ) for the oligosaccharides **1** - **3** calculated using a symmetrical top model ( $D_{\parallel}$ ,  $D_{\perp}$ ) and a fully anisotropic model ( $D_1$ ,  $D_2$ ,  $D_3$ ). For a bistable jump model,  $D_{\parallel}$  and  $D_{\perp}$  are overall diffusion constants assuming axially symmetric reorientation,  $D_1$  is diffusion constant for the jump between conformers **A** and **B**, and  $p_A$  denotes the population of conformer **A**. Glycosidic angles ( $\Phi, \Psi$ ) and ratios of the moment of inertia  $I_1:I_2:I_3$  represent structural features of the oligosaccharide conformers.

	<b>1 (A)</b>	<b>1 (B)</b>	<b>2 (A)</b>	<b>2 (B)</b>
( $\Phi, \Psi$ )	(-33°, -26°)	(-22°, 54°)	(34°, 29°)	(24°, -55°)
$I_1:I_2:I_3$	0.85:0.27:1.00	0.85:0.29:1.00	0.28:0.84:1.00	0.30:0.87:1.00
$D_{\parallel}$	2.2 $10^9$	2.1 $10^9$	2.2 $10^9$	2.1 $10^9$
$D_{\perp}$	2.0 $10^8$	2.1 $10^8$	2.4 $10^8$	2.3 $10^8$
$D_1$	2.3 $10^9$	1.7 $10^9$	2.3 $10^9$	0.9 $10^8$
$D_2$	1.4 $10^8$	3.3 $10^8$	1.8 $10^8$	3.2 $10^8$
$D_3$	2.8 $10^8$	6.9 $10^8$	3.4 $10^8$	2.3 $10^9$
$D_{\parallel}$	2.3 $10^9$		2.6 $10^9$	
$D_{\perp}$	4.0 $10^8$		3.4 $10^8$	
$D_1$	1.1 $10^8$		7.4 $10^8$	
$p_A$	0.33		0.56	
	<b>3 (A)</b>	<b>3 (B)</b>		
( $\Phi, \Psi$ )	(-40°, -30°)(21°, -54°)	(0°, 37°)(12°, -50°)		
$I_1:I_2:I_3$	0.57:0.60:1.00	0.62:0.55:1.00		
$D_{\parallel}$	7.8 $10^8$	7.5 $10^8$		
$D_{\perp}$	5.5 $10^8$	5.5 $10^8$		
$D_1$	2.6 $10^8$	6.7 $10^8$		
$D_2$	8.6 $10^8$	4.4 $10^8$		
$D_3$	6.7 $10^8$	7.0 $10^8$		
$D_{\parallel}$	3.0 $10^8$			
$D_{\perp}$	7.2 $10^8$			
$D_1$	4.9 $10^8$			
$p_A$	0.58			

A good fit was obtained between the majority of the calculated and experimental  $T_1$  values with use of the model of axially symmetric overall tumbling of a rigid molecule. However, the calculated  $T_1$  values for the transglycosidic carbons (Man C-1 and Glc C-2, and Rha C-1 and Glc C-3) are markedly larger than the experimental values, thus pointing to an additional relaxation path of these nuclei that was not taken into account in these calculations. A fully anisotropic model did not removed the deviations of the calculated relaxation times for the transglycosidic carbons. Therefore, a flexibility of glycosidic bonds in the studied oligosaccharides was taken into account using a bistable jump model allowing for segmental motions [4]. Exchange between two conformers differing in the geometry of glycosidic bonds was assumed. Their geometry resulted from the MM calculations. Including the internal motion we were able to fit calculated and experimental  $T_1$ s better than under assumption of the rigidity of whole molecule.

The results of calculations are presented in Table 1. They show that the motion about the glycosidic bonds is either comparable to or slower than the overall molecular tumbling. Comparing these results with those obtained for the internal rotation of the fucosyl residues in fucosylated lactoses [1] one can find that the latter exhibits motion at least one order of magnitude faster.

#### REFERENCES

- [1] A. Ejchart and J. Dabrowski, *Magn. Reson. Chem.*, **30**, S115 (1992).
- [2] A. Ejchart, T. Kozar, N.E. Nifant'ev, H. Grosskurth and J. Dabrowski, *Materiały XXVI Ogólnopolskiego Seminarium MRJ, Kraków 1994*, p. 196.
- [3] D.E. Woessner, *J. Chem. Phys.*, **37**, 647 (1962).
- [4] V.V. Krishnan, S.C. Shekar and A. Kumar, *J. Am. Chem. Soc.*, **113**, 7542 (1991).