

# Proton magnetic resonance spectroscopic studies in the presence of $\text{Eu}(\text{DPM})_3$ Conformations of some tetraacetyl-D-phenylglycosides

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Received 26 November 1973

The p.m.r. spectra of anomers of phenyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosides and D-galactopyranosides were measured. Comparison of coupling constants, as read from spectra recorded in the presence of  $\text{Eu}(\text{DPM})_3$  or without it, showed that the shift reagent did not influence the conformation of the six-membered ring.

Recently the use of some lanthanide complexes ( $\text{Eu}(\text{DPM})_3$ ,  $\text{Pr}(\text{DPM})_3$ ,  $\text{Eu}(\text{FOD})_3$ ) as so-called shift reagents has become of increasing importance; nevertheless only a few papers [1–6] refer to the application of this method to saccharides and their derivatives.

In our previous paper [6] we reported the effect of concentration and temperature of  $\text{Eu}(\text{DPM})_3$  on induced chemical shifts of some deoxy derivatives of saccharides. The conformation of these substances could not be estimated before addition of  $\text{Eu}(\text{DPM})_3$  since the p.m.r. spectrum was too complex and the coupling constants could not be properly read.

This paper deals with the effect of  $\text{Eu}(\text{DPM})_3$  on the magnitude of coupling constants and consequently, on the conformation of substances investigated, since the bulky molecule of the shift reagent might distort the six-membered ring.

## Experimental

The p.m.r. spectra were recorded with a Tesla BS-487 B 80 MHz spectrometer in  $\text{CDCl}_3$  (Merck), tetramethylsilane being the internal standard. Assignment of protons to signals of the spectrum was confirmed by the double-resonance technique.

Shift reagent  $\text{Eu}(\text{DPM})_3$  (Diaprep, Inc. Atlanta) was vacuum sublimed before use. The investigated substances: phenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranoside (*I*), phenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranoside (*II*), phenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-galactopyranoside (*III*), and phenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-galactopyranoside (*IV*) were prepared according to [7, 8]. Their physicochemical constants were in accordance with those reported.

## Results and discussion

The values of coupling constants,  $J$ , calculated from the p.m.r. spectrum measured in the presence of a shift reagent, are characteristic of the molecule (substrate—lanthanide complex) the conformation of which might be different from that recorded without it.

Substances under study have 5 active centres (4 oxygen atoms of acetyl groups and one oxygen atom of the pyrane ring) where the  $\text{Eu}(\text{DPM})_3$  complex could be attached.

Table 1

Coupling constants in the presence of  $\text{Eu}(\text{DPM})_3$  and without it

Com- pound	Without $\text{Eu}(\text{DPM})_3$ [Hz]*							With $\text{Eu}(\text{DPM})_3$ [Hz]*							Molar ratio $\text{Eu}(\text{DPM})_3$ / /saccharide
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	
<i>I</i>	3.5	10.0	9.7	9.7	—	—	—	4.0	10.2	9.7	9.7	4.8	2.0	12.0	0.20
<i>II</i>	—	—	—	9.0	5.2	2.5	12.5	7.7	9.5	9.0	9.2	5.5	2.6	12.0	0.54
<i>III</i>	3.0	10.5	3.2	1.0	—	—	—	3.0	10.5	3.5	1.0	6.2	6.3	11.0	0.44
<i>IV</i>	7.8	10.0	3.2	1.0	—	—	—	7.8	10.0	3.2	1.0	6.5	6.5	11.5	0.96

\* First order coupling constants  $J$  accurate to  $\pm 0.1$  Hz were taken directly from the spectra.

Table 1 lists coupling constants obtained in the presence of  $\text{Eu}(\text{DPM})_3$  or without it. As seen, the data obtained without the shift reagent are in favour of the C1 conformation of the investigated substances. The given molar ratio  $\text{Eu}(\text{DPM})_3/\text{saccharide}$  is the best for the separation of p.m.r. signals in the spectrum of the above-mentioned substances.

Coupling constants  $J_{5,6}$ ,  $J_{5,6'}$ ,  $J_{6,6'}$  of substances *I*, *III*, and *IV* could not be implied in the Table as we did not succeed to read them even though the INDOR technique was applied. On the other hand, these constants are of no substantial value when considering the conformation of the six-membered pyrane ring.

Figs. 1 and 2 show the most important changes in the p.m.r. spectrum of substances *I* and *II* after addition of  $\text{Eu}(\text{DPM})_3$ . When comparing values of the original coupling constants with those obtained after addition of the shift reagent it is evident that the majority of values is equal and the maximum difference amounts to  $+0.2-0.5$  Hz. This finding clearly evidences that the attachment of  $\text{Eu}(\text{DPM})_3$  to the molecules under

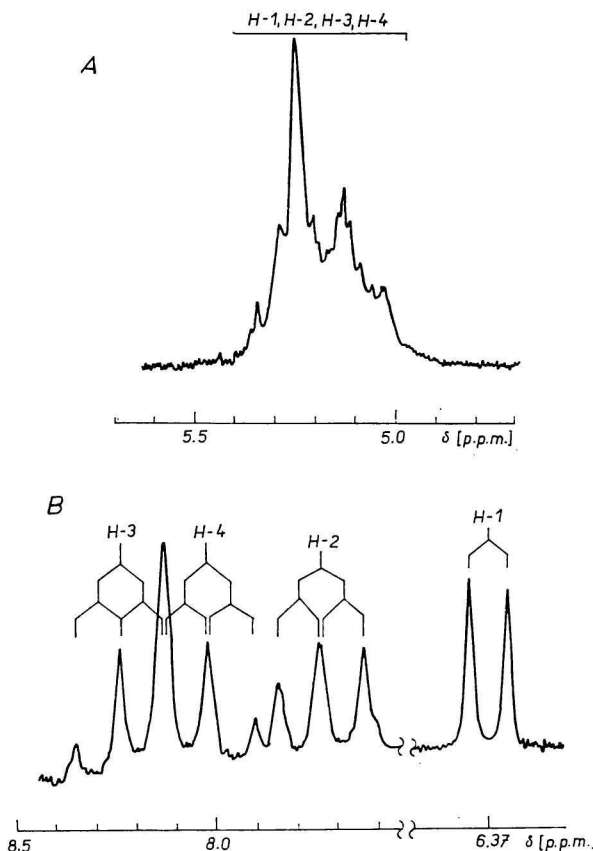


Fig. 1.

- A. The 80 MHz p.m.r. spectrum of phenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranoside.  
 B. The 80 MHz p.m.r. spectrum of phenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranoside in the presence of 0.54 molar ratio  $\text{Eu}(\text{DPM})_3/\text{saccharide}$ .

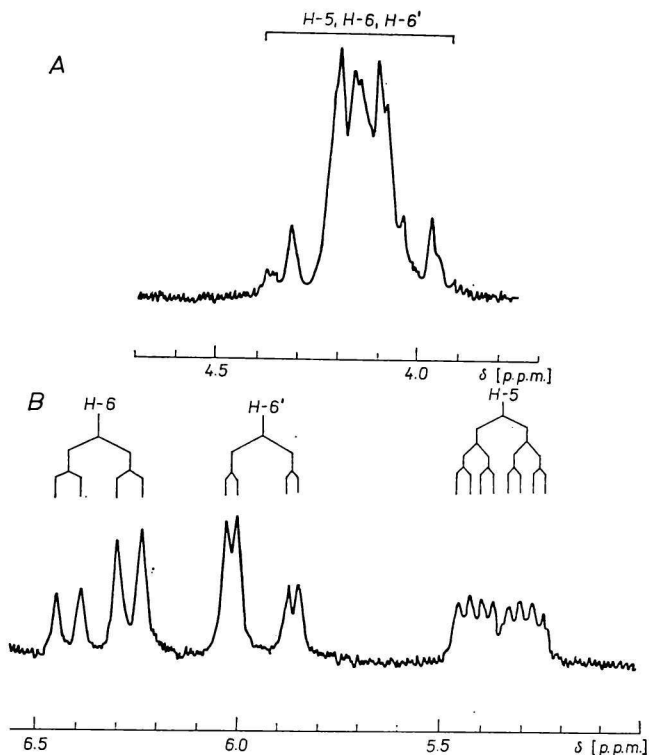


Fig. 2.

- A. The 80 MHz p.m.r. spectrum of phenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranoside.  
 B. The 80 MHz p.m.r. spectrum of phenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranoside in the presence of 0.33 molar ratio  $\text{Eu}(\text{DPM})_3/\text{saccharide}$ .

investigation does not result in distortion of the valence angles of the molecule, in other words, the stability of the C1 conformation of the six-membered ring remains unchanged.

One cannot, however, exclude the alteration of conformation of the molecule in unstable conformation systems caused by the shift reagent; a more detailed study of this problem is in progress.

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Translated by Z. Votický