Conformational study of aldobiouronic acids by means of proton magnetic resonance spectrometry

C. PECIAR, J. ALFÖLDI, R. PALOVČÍK, J. ROSÍK, and J. KUBALA

Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava

Received 20 March 1973

Chemical shifts and coupling constants $J_{1,2}$ of anomeric protons of three aldobiouronic acids were measured. Basing on the data obtained the configuration of the glycosidic bond was determined. The relative abundance of the respective anomers in the equilibrated mixture was established from the area of peaks of anomeric protons at the reducing unit.

It has been reported [1] that the p.m.r. signals of anomeric protons of aldohexapyranosides are more downfield shifted than those of other protons, what can be useful when determining the configuration of glycosidic bonds of oligosaccharides. Anomeric protons in equatorial position were found to be more deshielded than those in the axial position due to the interaction with the *p*-orbital of the ring-oxygen [2, 3]. In general, the value of the vicinal coupling constant depends on the mutual position of the interacting protons.

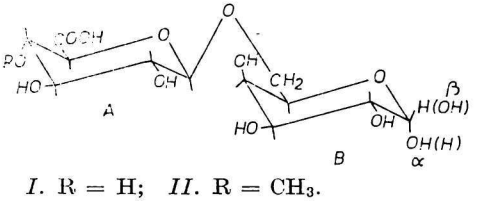
The axial-equatorial and equatorial-equatorial coupling between protons at C-1 and C-2 is 1—4 c.p.s. whereas that of axial-axial 7—9 c.p.s.

The use of p.m.r. spectrometry in the structure elucidation of oligosaccharides is rather limited due to almost the same distribution of functionalities in their molecules. Nonetheless, papers so far published, namely [2—6], show that p.m.r. spectrometry could successfully be employed in the structure determination of oligosaccharides.

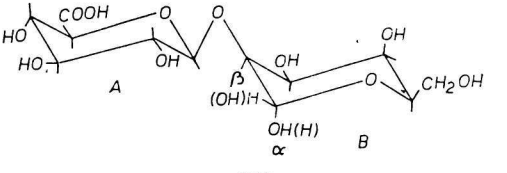
This paper refers to the estimation of the configuration of the glycosidic bond of 6-*O*-(β-D-glucuronopyranosyl)-D-galactopyranose (*I*), 6-*O*-(4-*O*-methyl-β-D-glucuronopyranosyl)-D-galactopyranose (*II*), and 2-*O*-(β-D-glucuronopyranosyl)-D-mannopyranose (*III*).

Results and discussion

Chemical shifts of protons at anomeric carbons in reducing and nonreducing rings of compounds *I*, *II*, and *III* (Scheme 1) display various values depending on the configuration of the glycosidic bond and the reducing unit.



I. R = H; *II*. R = CH_3.



III.

Scheme 1

The different chemical shift of protons of the same type in rings *A* and *B* is evidently subject to the different effect of the magnetic anisotropy of glycosidic bond at both rings.

All three substances under study reveal signals of anomeric axially oriented protons of nonreducing rings *A* within the δ 4.53—4.58 region. Signals of equatorially oriented protons of reducing rings *B* are downfield shifted and appear at δ 5.24—5.27. It is noteworthy that signals of anomeric axially oriented protons of both reducing and nonreducing moiety of the molecule of substances *I* and *III* occur at the same value and substance *II* differs only slightly (0.03 p.p.m.).

Table 1

δ Values and coupling constants of anomeric protons in c.p.s.

Compound	Chemical shift			Coupling constant $J_{1,2}$		
	Nonreducing ring	Reducing ring		Nonreducing ring	Reducing ring	
		equat.	axial		equat.	axial
I	4.58	5.25	4.58	7.70	2.90	7.70
II	4.53	5.24	4.56	7.50	2.90	7.30
III	4.58	5.27	4.58	7.50	1.10	4.40

The spin-spin coupling constant between protons at C-1 and C-2 of nonreducing ring *A* of substances *I*, *II*, and *III* was found to be 7.5—7.7 c.p.s., this being indicative of an axial-axial coupling and hence for a β-glycosidic bond (Table 1). Moreover, two doublets of lower intensity were observed in the respective spectra: one belonging to the β-H (ring *B*) at δ 5.24—5.27 ($J_{1,2}$ = 1.1—2.9 c.p.s.), the other at δ 4.56—4.58 ($J_{1,2}$ = = 4.4—7.70 c.p.s.) is characteristic of axial-equatorial and axial-axial coupling and also of a terminal reducing group — mannose — in the oligosaccharide *III*.

It has been estimated, basing upon the area of the resonance peaks, that in an equilibrated mixture the α and β anomers are in a 1 : 1 ratio in compounds *I* and *II* and 1 : 5 in compound *III* in favour of the α anomer.

Experimental

Aldobiouronic acids *I*, *II*, and *III* were prepared by partial acid hydrolysis of the polysaccharide isolated from the peach-tree gum of *Prunus persica* (L.) BATSCH. [7—9]. All substances were identical with specimens and were measured as 15% solutions in D_2O with a Tesla BS-487-B spectrometer at 80 Mc, sodium 4,4-dimethyl-4-silapentane sulfonate (DSS) being the internal reference substance. The area of peaks measured with a p.m.r. integrator was accurate to ±5%.

References

1. Van der Veen, J. M., *J. Org. Chem.* ***28***, 564 (1972).
2. Lemieux, R. U., Kulling, R. K., Bernstein, H. J., and Schneider, W. G., *J. Amer. Chem. Soc.* ***80***, 6098 (1958).
3. Kamerling, J. P., de Bie, M. J. A., and Vliegenthart, J. F. G., *Tetrahedron* ***28***, 3037 (1972).

4. Isakov, V. V., Dzizenko, A. K., Govorchenko, V. I., Denisenko, V. A., and Ovodov, Yu. S., *Khim. Prirod. Soedin.* ***4***, 425 (1972).
5. Suami, T., Otake, T., Ogawa, S., Shoji, T., and Kato, N., *Bull. Chem. Soc. Jap.* ***43***, 1219 (1970).
6. Gasu, B. and Reggiani, M., *Carbohyd. Res.* ***12***, 157 (1970).
7. Rosík, J., Bruteničová-Sósková, M., Zitko, V., and Kubala, J., *Chem. Zvesti* ***20***, 577 (1966).
8. Rosík, J., Zitko, V., and Kubala, J., *Chem. Zvesti* ***19***, 931 (1965).
9. Rosík, J., Kardošová, A., and Kubala, J., *Chem. Zvesti* ***21***, 739 (1967).

Translated by Z. Votický