A STUDY OF THE ^{1}H NMR SPECTRA OF OCTAACETATES OF DISACCHARIDES

V. V. Isakov, A. K. Dzizenko,
V. I. Govorchenko, V. A. Denisenko,
and Yu. S. Ovodov

UDC 538.113 + 547.917

The development of structural methods of investigating oligosaccharides is of great importance both for the chemistry of the oligo- and polysaccharides and for the study of carbohydrate-containing biopolymers. The use of NMR spectroscopy for structural investigations of oligosaccharides is not yet sufficiently widespread. The great uniformity of the functional composition of the oligosaccharides complicates the solution of the problem faced. It is mainly the signals of the protons on the C_1 atoms that have been studied by means of ^{1}H NMR spectra [1]. An investigation of the signals of the protons attached to the C_2-C_6 atoms, which has been performed for a number of oligosaccharides [2] and their acetates [3], shows the possibility of using ^{1}H NMR spectroscopy for the identification and structural determination of oligosaccharides.

We have analyzed the spectra of octaacetates of disaccharides (α,α-trehalose, α-kojibiose, β-kojibiose, β-sophorose, O-α-D-glucopyranosyl-(1→)-β-D-galactose, β-laminaribiose, β-maltose, β-cellobiose, and β-gentiobiose), with different positions (1→1, 1→2, 1→3, 1→6) and configurations of the glycosidic linkage. The spectra were recorded at the ordinary temperature in $CDCl_3$ on Varian HA-100 and JNM-4H-100 instruments. The chemical shifts (CSs) were measured in the δ scale, tetramethylsilane (TMS) being used as internal standard. The samples studied were synthesized by the usual methods [4]; their constants corresponded to those given in the literature.

On considering the NMR spectra of the octaacetates of the disaccharides (Figs. 1 and 2), it can be seen that the CSs of the signals of the corresponding protons of the nonreducing ring (A) and of the reducing ring (A_1) have different values and depend on the configuration of the glycoside linkage and of the reducing ring. The difference in the CSs of monotypical protons of rings A and A_1 is due to the dissimilar influences of the magnetic anisotropy of the glycosidic linkage (C−O−C) and of the acetoxy group at the C_1 atom of ring A_1. A comparison of the CSs in the spectra of the octaacetates of the disaccharides (Table 1), of α-D-glucose pentaacetate, and of α-D-glucose 1,3,4,6-tetraacetate (Table 2) shows that the signal of the proton at a C atom to which an acetoxy group is attached is shifted downfield by $\Delta\delta$ 1.0 ppm. The protons on the anomeric carbon atom of the reducing ring appear in the form of signals of the other protons. In all cases, the axial protons of the reducing ring (H-1') of the octaacetates of β-glucobioses give a doublet ($J \simeq 8.0$ Hz) at δ 5.6-5.7 ppm, and the equatorial protons (H-1') of the octaacetates of α-glucobioses give a doublet ($J \simeq 4.0$ Hz) at δ 6.30-6.40 ppm. The difference in the CSs ($\Delta\delta$ 0.4 ppm) of the axial and equatorial protons can be used to determine the configurations of the glycosidic center of the reducing ring of a disaccharide.

The absence of an acetoxy group from the anomeric carbon atom of the nonreducing ring leads to an upfield shift of the proton at the C_1 atom. Thus an axial H-1 proton (β-glycosidic linkage) gives a signal at δ 4.5-4.8 ppm with a spin−spin coupling constant (SSCC) J = 8.0 Hz, and an equatorial H-1 proton (α-glycosidic linkage) gives a signal at δ 5.2-5.4 ppm with a SSCC J = 4.0 Hz. The different values of the CSs of the anomeric protons of the reducing and the nonreducing rings and the SSCCs enable the configurations of the glycosidic linkages in the disaccharides to be established (Table 3). The protons on the C_2-C_4 atoms

Institute of Biologically Active Substances, Far-Eastern Scientific Center, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 425-430, July-August, 1972. Original article submitted January 18, 1972.

TABLE 1. Chemical Shifts* (δ, ppm) and SSCCs (Hz) of the Ring Protons of the Octaacetates of Disaccharides with Different Types of Glycosidic Linkage

Compound	Ring	Protons					
		H_1	H_2	H_3	H_4	H_5	2 H_6
α,α-Trehalose	A	5,28 (3,8)	5,01 (3,8; 9,7)	5,48 (9,7; 9,7)	5,02 (9,7; 9,7)	3,90–4,40	3,90–4,40
$A\frac{C\dagger}{2}A_1$	A_1	5,28 (3,8)	5,01 (3,8; 9,7)	5,48 (9,7; 9,7)	5,02 (9,7; 9,7)	3,90–4,40	3,90–4,40
α-Kojibiose	A	5,14 (3,4)	4,91 (3,4; 9,8)	5 34 (9,8; 10,0)	5,06 (10,0; 9,6)	3,80–4,50	3,80–4,50
$A\frac{C}{2}A_1$ (α)	A_1	6,34 (4,0)	3,97 (4,0; 10,0)	5,49 (10,0; 10,0)	5,15 (10,0; 9,4)	3,80–4,50	3,80–4,50
β-Kojibiose	A	5,48 (3,6)	4,74 (8,6; 9,5)	4,31 (9,5; 9,7)	5,02 (9,7; 10,0)	3,60–4,50	3,60–4,50
$A\frac{C}{2}A_1$ (β)	A_1	5,69 (8,0)	3,89 (8,0; 8,9)	5,31 (8,9; 9,6)	5,03 (9,6; 9,8)	3,60–4,50	3,60–4,50
β-Sophorose	A	4,64 (7,8)	4,90 (7,8; 9,0)	5,21 (9,0; 9,0)	5,01 (9,0; 9,0)	3,50–4,50	3,50–4,50
$A\frac{T}{2}A_1$ (β)	A_1	5,71 (8,0)	3,86 (8,0; 8,7)	5,27 (8,7; 8,7)	5,11 (6; 8,7)	3,50–4,50	3,50–4,50
O-α-β-Glucopyranosyl-(1→2)-β-D-glucose	A	4,65 (8,0)	4,92 (8,0; 9,0)	5,19 (9,0; 9,0)	5,13 (9,0; 9,0)	3,50–4,40	3,50–4,40
$A\frac{T}{2}A_1$ (α)	B	6,36 (3,5)	4,07 (3,5; 8,6)	5,37 (8,6; 3,7)	5,44 (3,7; 9,7)	3,50–4,40	3,50–4,40
β-Laminaribiose	A	4,62 (7,8)	4,90 (7,8; 9,0)	5,14 (9,0; 9,0)	5,03 (9,0; 9,0)	3,60–4,50	3,60–4,50
$A\frac{C}{3}A_1$ (β)	A_1	5,65 (8,0)	4,98 (8,0; 8,5)	3,94 (8,5; 9,0)	5,11 (9,0; 9,0)	3,60–4,50	3,60–4,50
β-Maltose	A	5,41 (3,5)	4,85 (3,5; 1,1)	5,34 (11; 8,7)	5,01 (8,7–9,0)	3,80–4,60	3,80–4,60
$A\frac{C}{4}A_1$ (β)	A_1	5,72 (8,0)	4,92 (8,0; 8,5)	5,27 (8,5; 8,5)	4,01 (8,5; 8)	3,80–4,60	3,80–4,60
β-Cellobiose	A	4,53 (7,5)	4,32 (7,5; 8,5)	5,15 (8,5; 9,0)	5,03 (9,0; 8,5)	3,70–4,50	3,70–4,50
$A\frac{1}{4}A_1$ (β)	A_1	5,68 (8,0)	4,95 (8,0; 7,8)	5,24 (7,8; 8,5)	4,11 (8,5; 8,7)	3,70–4,50	3,70–4,50
β-Gentiobiose	A	4,55 (7,6)	4,94 (7,8; 8,8)	5,20 (8,8; 8,8)	5,03 (8,8; 9,0)	3,30–4,40	3,30–4,40
$A\frac{C}{6}A_1$ (β)	A_1	5,69 (7,5)	4,96 (7,5; 8,8)	5,25 (8,8; 8,8)	5,16 (8,8; 9,0)	3,30–4,40	3,30–4,40

*Accuracy of the measurement of the CSs ±0.02 ppm and of the SSCCs ±0.5 Hz.

†For an explanation of the magnitudes $A\frac{C}{1}$ and $A\frac{C}{2}$, etc., see [2].

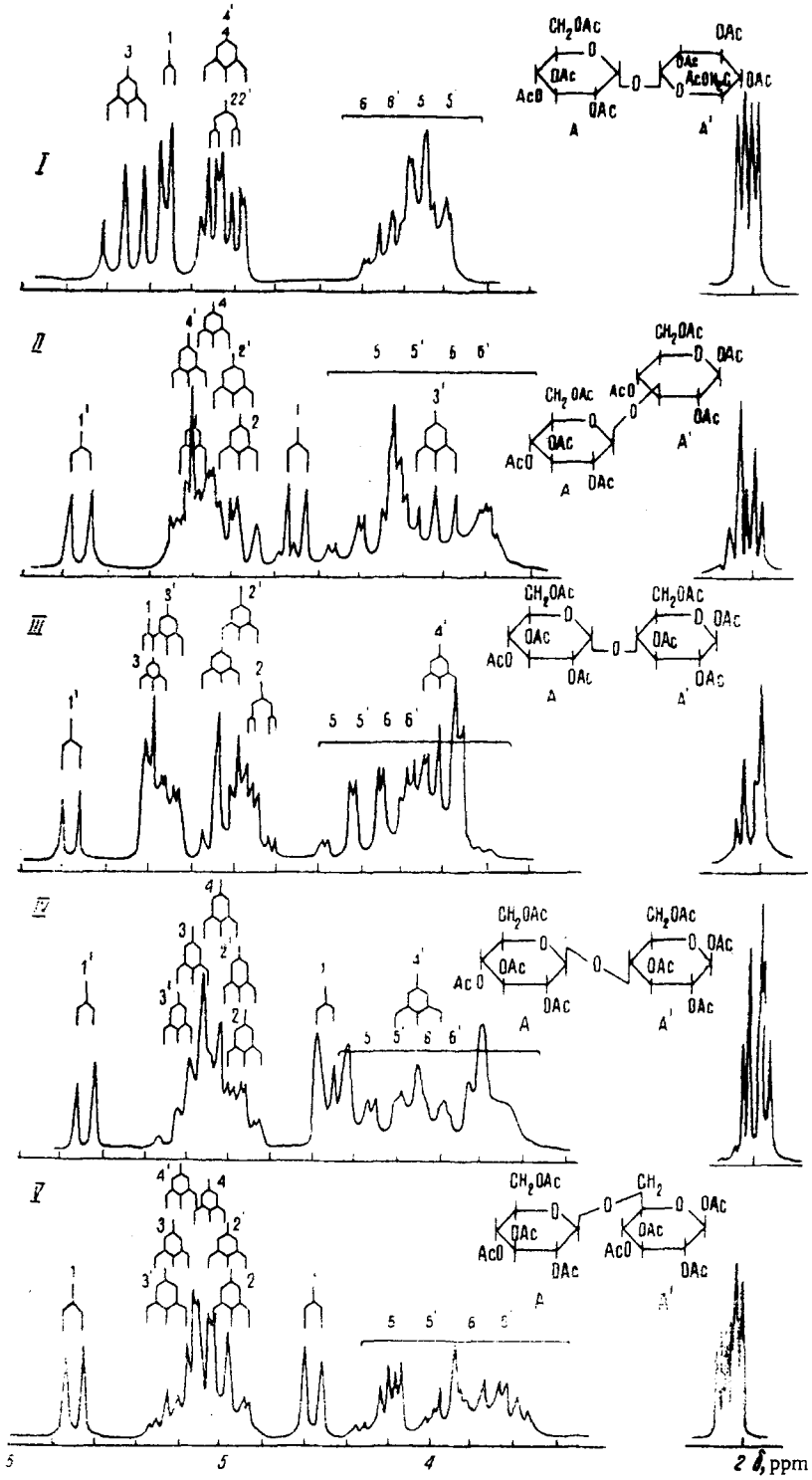

Fig. 1. NMR spectra of octaacetates of the following glucobioses I) α,α-trehalose; II) β-laminaribiose; III) β-maltose; IV) β-cellobiose; V) β-gentiobiose.

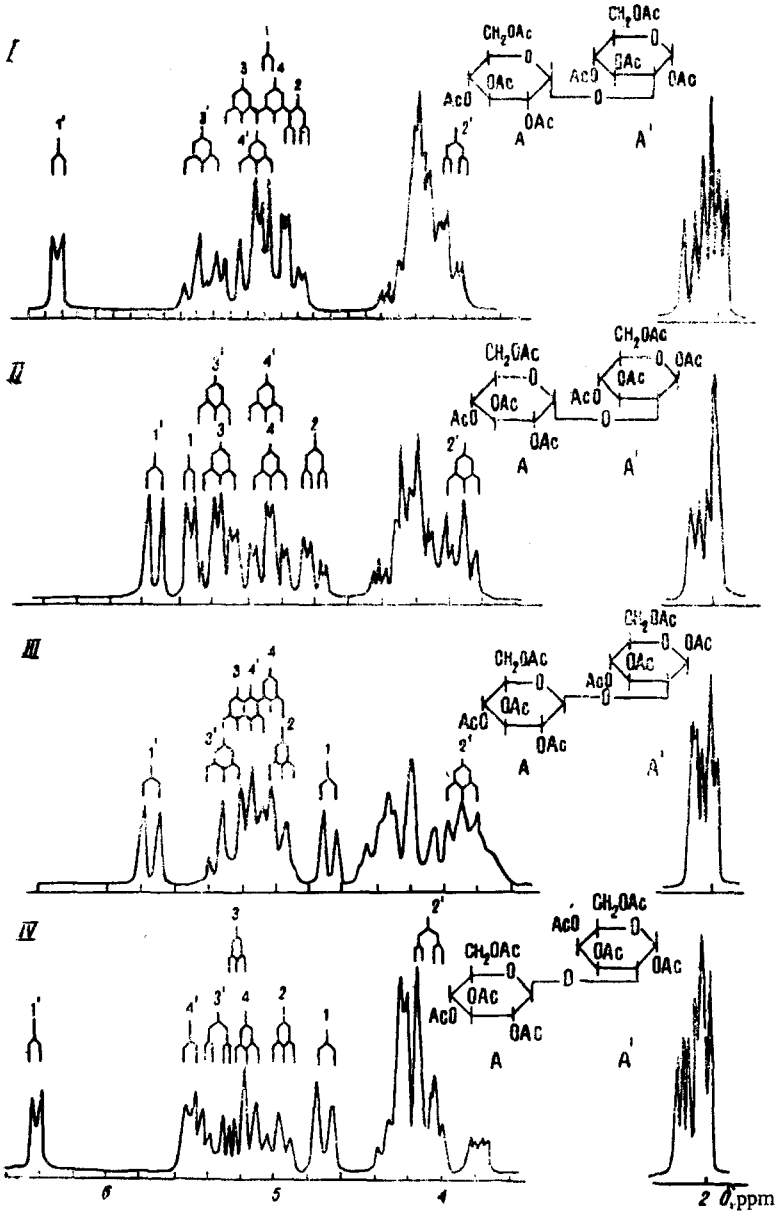

Fig. 2. NMR spectra of octaacetates of disaccharides with a 1,2-glycosidic linkage: I) α-kojibiose; II) β-kojibiose; III) β-sophorose; IV) O-α-D-glucopyranosyl-(1→2)-β-D-galactose.

TABLE 2. Chemical Shifts of the Protons (δ, ppm) and SSCCs (Hz) of Acetylated Monosaccharides

Acetylated α-D-glucose derivatives	Protons			
	H-1	H-2	H-3	H-4
1,2,3,4,6-Penta-	6,31 (4,0)	5,08 (4,0; 9,8)	5,49 (9,9; 9,8)	5,13 (9,8; —)
1,3,4,6-Tetra-	6,16 (3,5)	3,90 (3,5; 9,5)	5,22 (9,5; 9,5)	4,98 (9,5; —)

TABLE 3. Information for the Determination of the Configurations of the Glycosidic Bonds

δ, ppm, and J, Hz		Δδ (H1'–H1)	Configuration of the glycosidic bond	
H-1'	H-1		reducing ring	non-reducing ring
6,30–6,40 (3,5–4,0)	5,20–5,40 (3,5–4,0)	~1,0	α	α
6,30–6,40 (3,5–4,0)	4,50–4,80 (7,5–8,0)	~1,7	α	β
5,60–5,70 (7,5–8,0)	5,20–5,40 (3,5–4,0)	~0,4	β	α
5,60–5,70 (7,5–8,0)	4,50–4,80 (7,5–8,0)	~0,9	β	β

of rings A and A_1, not participating in the formation of the glycosidic linkage, give signals in the region of δ 4.7-5.40 ppm and partially overlap one another (a clear separation of the signals is observed in β-kojibiose). Analysis of the spectra, their comparison, and the use in some cases of the decoupling method has permitted an assignment of the signals of these protons to be made (see Table 1). It can be seen from Table 3 that the signals of the protons are arranged in the following sequence: H-2,2'; H4,4'; H-3,3', i.e., in the direction of decreasing field strength.

The use of this relationship, taking into account the shift of the proton participating in the formation of the glycosidic linkage upfield by $\Delta\delta$ 1 ppm, makes it possible to determine the position of the glycosidic linkage from the nature of the intensities of the signals of the protons on the C_2-C_4 atoms in the δ 4.7-5.40 ppm region. In the case of a 1→6 glycosidic linkage, a difference in the CSs of the protons on the C_6 atom of the rings A and A_1 is characteristic. The protons on the C_6 atom of the nonreducing ring (A) appear in the form of a multiplet with its center at δ 4.10 ppm, and the signals of the protons at the C_6 atom of the reducing ring (A_1) appear in the form of a multiplet at δ 3.70 ppm. For this case, the difference in the screening of the acetoxy group and the glycosidic linkage is $\Delta\delta$ 0.4 ppm.

From the CS of the signal of the proton at the C_2 atom of ring A and its nature, it is possible to obtain additional information on the configuration of the glycosidic linkage. Thus, for the α configuration of the glycosidic linkage, the signals of the protons at C_2 have the form of a quartet with δ 4.8 ppm, and for the β configuration they form a triplet with δ 4.90 ppm. A difference is also observed in the CSs of the signals at the C_3 atom for the α and β anomers ($\Delta\delta$ 0.1 ppm).

SUMMARY

1. The ^{1}H NMR spectra of octaacetates of disaccharides with different positions (1→1, 1→2, 1→3, 1→4, and 1→6) and configurations of the glycosidic bonds have been studied.

2. The possibility has been shown of determining the position and configuration of the glycosidic bonds from ^{1}H NMR spectra of disaccharide octaacetates.

LITERATURE CITED

1. J. M. Van der Veen, J. Org. Chem., 28, 564 (1963); C. A. Glass, Can. J. Chem., 43, 2652 (1965).
2. Yu. S. Ovodov and A. K. Dzizenko, Dokl. Akad. Nauk SSSR, 178, 1348 (1968).
3. W. W. Binkley, D. Horton, and N. S. Bhacca, Carbohyd. Res., 10, 245 (1969); B. Gasu, M. Reggiani, G. Gallo, and G. Vigevani, Carbohyd. Res., 12, 15 (1970);M. Matsui and M. Okada, Chem. Pharm. Bull., 19, 395 (1971).
4. D. D. Reynolds and W. L. Evans, J. Amer. Chem. Soc., 60, 2559 (1938); B. H. Kolppen, Carbohyd. Res., 7, 410 (1968); B. Helferich and J. Zirner, Chem. Ber., 95, 2604 (1964); L. Bachli and E. G. V. Percival, J. Chem. Soc., 1243 (1952).