A STUDY OF ACETYLATED GLYCOSIDES AND MALTOSIDES OF SOME STEROIDS BY THE ^{1}H-NMR METHOD

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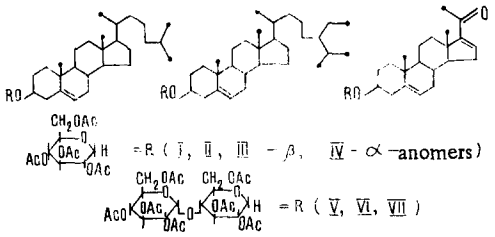
Thanks to the successful use of the ^{1}H-NMR method in determining the structures of mono- and oligosaccharides [1-3], at the present time it has become possible to study the structure of the carbohydrate moiety of a glycoside. The investigation of the NMR spectra of model glycosides with several monosaccharide residues is of great importance. This can give valuable information both on the structure of the carbohydrate moiety of the glycosides and also on the influence of the carbohydrate component on the aglycone, which will enable the results of NMR spectroscopy to be used in subsequent structural investigations of more complex natural glycosides.

The literature refers mainly to information on the signal of the anomeric proton in glycosides with one monosaccharide residue [4-6].

The present paper gives the results of a consideration of the NMR spectra of the acetylated glycosides and maltosides of a number of steroids in order to find characteristic features of the behavior of the signals of all the ring protons of the carbohydrate part of the molecule.

We have studied the spectra of acetylated mono- and diglucopyranosides of cholesterol, β-sitosterol, and 16-dehydropregnenolone. The chemical shifts, δ (CSs) and spin–spin coupling constants (Hz) of the signals of the protons of the carbohydrate moieties of the glycosides are given in Table 1.



In the spectra of compounds (I-VII) the signals of the protons of the aglycone are mainly found in the $\delta = 0.5$-2.0 ppm region and the signals of the protons of the carbohydrate moiety in the $\delta = 3.5$-5.5 ppm region, which makes it possible to perform a complete analysis of the signals of the protons of the carbohydrate moiety (see Table 1). Thus, in the NMR spectrum of compound (I) (Fig. 1, a), the signal of the proton on the C-1 atom of the glucose residue appears at $\delta = 4.60$ ppm with a spin–spin coupling constant (SSCC), $J_{1,2} = 8.0$ Hz. Such values of the CS and the SSCC [5] show the β configuration of the glycosidic linkage. In the spectrum of compound (IV) (Fig. 1, b), the signal of the proton on the C-1 atom appears at $\delta = 5.25$ ppm with a SSCC $J_{1,2} = 3.5$ Hz, which shows the α configuration of the glycosidic bond [5]. On comparing the NMR spectra of compounds (I) and (IV) (Fig. 1a and b), it can be seen that a change in the configuration of the glycosidic bond from β to α leads to a change in the CSs and SSCCs not only of the signal of the proton attached to the glycosidic carbon atom but also of the signals of the ring protons on the C_2-C_6

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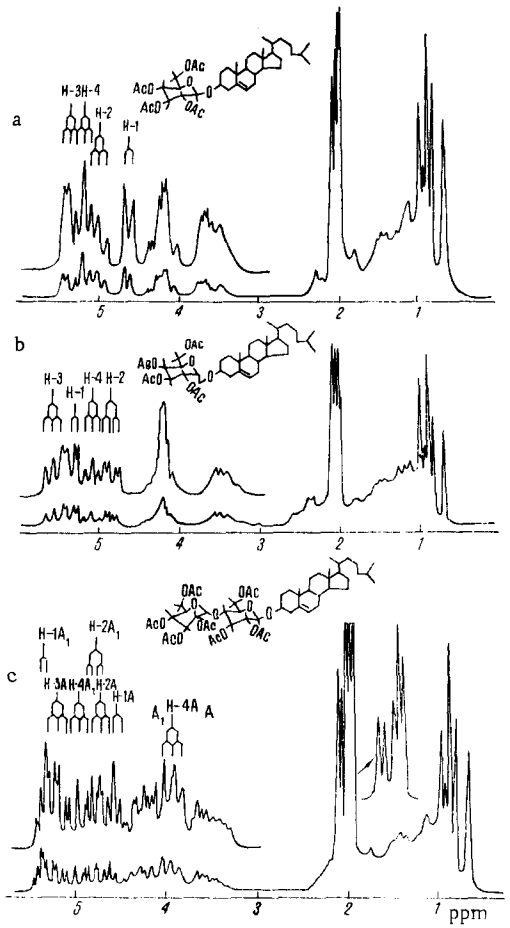

Fig. 1. NMR spectra of acetylated glycosides: the β-D-glucopyranoside of cholesterol (a), the α-D-glucopyranoside of cholesterol (b), and the β-maltoside of cholesterol (c).

TABLE 1

Compound	Ring†	Protons*					
		H-1	H-2	H-3	H-4	H-5	2H-6
I	A	4,60 (8,0)	4,97 (8,0; 8,0)	5,24	5,16	3,68 ‡(m)	4,22(*m*)
II	A	4,59 (7,9)	4,93 (7,9; 8,0)	5,21	5,12	3,70(*m*)	4,20(*m*)
III	A	4,60 (7,9)	4,96 (7,9; 8,0)	5,30	5,08	3,65(*m*)	4,20(*m*)
IV	A	5,25 (3,9)	4,81 (3,9; 9,8)	5,50	5,06	3,90(*m*)	4,20(*m*)
V	A	4,60 (8,0)	4,72 (8,0; 8,0)	5,27	3,97	—	—
	A_1	5,39 (3,5)	4,84 (3,5; 10,0)	5,35	5,02	—	—
VI	A	4,59 (8,0)	4,78 (8,0; 8,0)	5,25	3,98	—	—
	A_1	5,40 (3,5)	4,83 (3,5; 10,0)	5,37	5,03	—	—
VII	A	4,64 (8,0)	4,83 (8,0; 8,0)	5,28	3,92	—	—
	A_1	5,40 (3,6)	4,87 (3,6; 9,9)	5,44	5,06	—	—

*The NMR spectra were recorded on a Varian HA-100D instrument in $CDCl_3$.

†A – monosaccharide ring connected with the genin by a glycosidic bond; A_1 – monosaccharide ring connected with ring A.

‡m – center of a multiplet.

atoms of the monosaccharide residue. For example, while in the spectrum of the tetraacetate of the β-D-glucopyranoside of cholesterol (I) (see Fig. 1a), the signal of the proton on the C-2 atom has a triplet nature ($\delta = 4.97$ ppm) and the CSs of the signals of the protons on the C-3 and C-5 atoms are $\delta = 5.25$ and 3.65 ppm (center of a multiplet), respectively, in the tetraacetate of the α-D-glucopyranoside of cholesterol (II) the signal of the proton on the C-2 atom forms a quartet and is shifted upfield by $\Delta\delta = 0.16$ ppm and the signal of the proton on the C-3 atom is shifted downfield by $\Delta\delta = 0.26$ ppm through the deshielding effect of the glycosidic bond. The regions of the signals of the protons on the C-6 atom also differ (AB part of a ABX system in the case of a β-glycosidic bond and the AB part of a ABC-system in the case of an α-glycosidic bond. Similar features are observed in the behavior of the signals of the protons of the monosaccharide moieties in the spectra of the tetraacetates of the glucopyranosides of β-sitosterol and 16-dehydropregnenolone (see Table 1).

With an increase in the number of monosaccharide residues in the glycoside to two (maltose) in the assignment of the signals of the protons, it is necessary to distinguish between the monosaccharide residues A and A_1 (Fig. 1c). The results obtained above and literature information [4] enable the signals of the protons of the two rings to be distinguished (see Table 1). Thus, in the NMR spectrum of the heptaacetate of the maltoside of cholesterol (see Fig. 1c), the signal of the proton at the C-1 atom of ring A appears in the form of a doublet at $\delta = 4.60$ ppm with an SSCC of $J_{1,2} = 8.0$ Hz, and the signal of the C-2 proton at $\delta = 4.72$ ppm, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 8.0$ Hz, and has a triplet nature. This shows the β configuration of the glycosidic bond of the monosaccharide ring A with the aglycone. At the same time, the signal of the C-1 proton of ring A_1 appears at $\delta = 5.40$ ppm, $J_{1,2} = 3.5$ Hz, and the signal of the C-2 proton in the form of a quartet at $\delta = 4.84$ ppm, with SSCCs of $J_{2,1} = 3.5$ Hz and $J_{2,3} = 10.0$ Hz, which confirms the α configuration of the glycosidic bond between the monosaccharide residues.

Similar characteristic features are observed in the spectra of the heptaacetates of the maltosides of β-sitosterol and of 16-dehydropregnenolone (see Table 1).

We are making a similar investigation of triterpene glycosides. Here, in addition to those described above, definite characteristic features of the influence of the anisotropy of the glycosidic bond on the CSs of the signals of the Me groups of the genin are observed.

SUMMARY

The possibility of determining the configuration of the glycosidic bond in acetylated mono- and diglucopyranosides of steroids by an analysis of the signals of all the protons of the monosaccharide residues has been shown.

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