^{13}C NMR SPECTRA OF ACETYLATED METHYL GLYCOSIDES OF MONOSACCHARIDES

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There is voluminous information in the literature on the ^{13}C spectra of free monosaccharides and their methyl esters [1, 2] which makes it possible to investigate oligo- and polysaccharides by ^{13}C spectroscopy. The information on the spectra of acetylated sugars is of incomplete nature [1, 3-5]. At the same time, acetylated derivatives of monosaccharides may be extremely useful in the study of the oligosaccharide part of glycosides in view of the specific problems arising in obtaining spectra of glycosides in such solvents as pyridine or dimethyl sulfoxide (broadening of the lines of the methine and methylene carbon atoms, superposition of the signals of the solvent).

In this paper we give information on the ^{13}C NMR spectra of the acetates of methyl glycosides of a number of monosaccharides (Table 1 and Scheme 1). The signals were assigned by the method of selective decoupling from protons using solvents with different polarities (C_6D_6, $CDCl_3$, $(CD_3)_2CO$) and literature information on the ^{1}H NMR spectra [6, 7]. A distinction between the C_3 and C_4 signals in the spectrum of the acetate of methyl α-Me-D-fucopyranoside was made on the basis of the comparative smallness of the shift of the latter on its anomerization [3].

It can be seen from the facts given that the range of chemical shifts of the C_2-C_6 atoms (excluding C_6 of 6-deoxyhexoses) in the case of the acetates (12.7 ppm) is somewhat less than for the free methyl glycosides (14.8 ppm), which shows in general, a smaller degree of informativeness of the spectra of the acetylated oligosaccharides.

Anomerization ($H_{1ax} \rightarrow H_{1eq}$) shifts the C_3 and C_5 signals upfield by approximately the same amount as in the unsubstituted methyl glycosides [1], while the C_2 shifts, although they retain their sign, are far smaller: −0.4, 0.1, −0.7, −0.9, and −0.7 ppm in (I-X) and −1.7, −1.7, −2.4, −2.4, and −2.5 ppm in the corresponding unsubstituted compounds.

TABLE 1. ^{13}C Chemical Shifts of Acetylated Methyl Glycosides (ppm)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C=O		OCH_3	$OCOCH_3$
β-Me-*D*-Glu	101,6	71,3	72,9	68,5	71,8	61,9	170,2 170,4	169,3 169,9	56,9	20,6
α-Me-*D*-Glu	98,9	70,9	70,2	68,7	67,3	62,1	169,5		55,4	20,6
β-Me-*D*-Xyl	101,8	71,0	71,7	69,1	62,1		170,0		56,5	20,7
α-Me-*D*-Xyl	97,0	71,1	69,7	69,4	58,2		169,9	170,0	55,4	20,7
β-Me-*D*-Gal	102,1	68,9	71,0	67,1	70,7	61,3	170,3	169,6	56,9	20,6
α-Me-*D*-Gal	97,2	68,2	67,6	68,2	66,2	61,7	170,2	169,7	55,4	20,6
β-Me-*L*-Ara	97,6	68,4	67,2	69,3	60,2		170,3	170,0	55,6	20,9
α-Me-*L*-Ara	102,0	69,3	70,4	67,9	63,2		170,0	169,4	56,6	20,8
β-Me-*L*-Fuc	101,9	69,0	71,5	70,3	69,1	16,0	170,5 169,4	170,1	56,7	20,6
α-Me-*L*-Fuc	97,3	68,3*	68,0*	71,3	64,3	15,9	170,5 169,9	170,1	55,4	20,7
β-Me-*L*-Rha	99,5	69,0	71,2	70,8	70,6	17,4	170,3 169,7	169,7	57,2	20,7
α-Me-*L*-Rha	98,5	69,8	69,2	71,0	66,3	17,4	169,7	169,4	55,0	20,7

* The values of these shifts may be interchanged.

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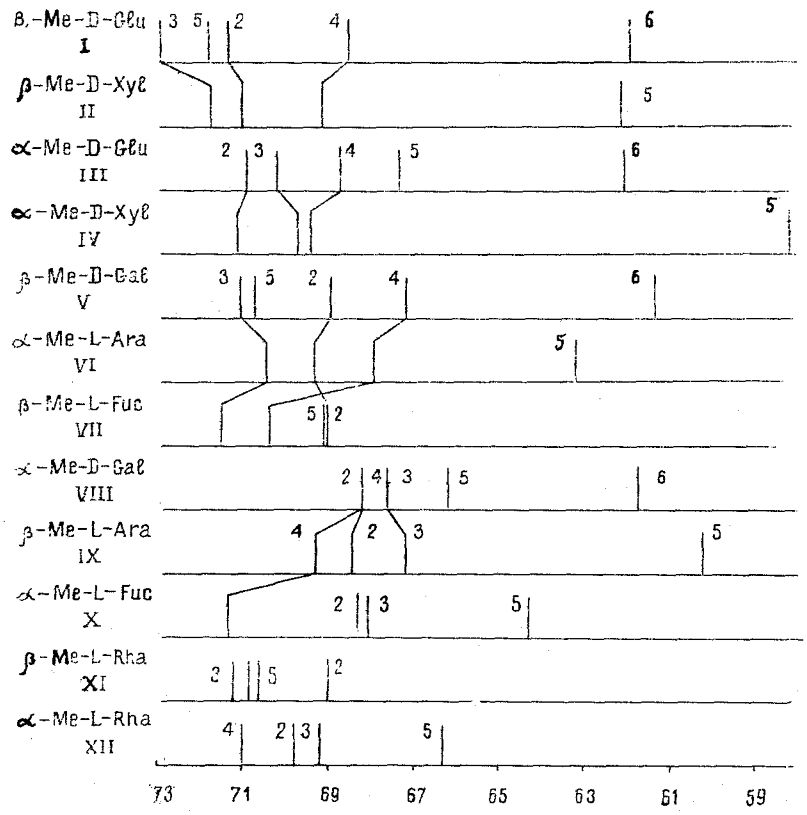

Scheme 1. Correlation of the ^{13}C chemical shifts of acetylated methyl glucosides.

On the other hand, on passing from methyl hexosides to the corresponding pentosides and 6-deoxyhexosides in the cases of (II) and (IV) there are shifts in the C_3 signals by −1.2 and −0.5 ppm and for (VII) and (X) a shift in the C_3 signal and for (VI) and (IX) in the C_2 signal by 0.5, 0.4, 0.4, and 0.2 ppm, respectively as compared with no or considerably smaller shifts in the spectra of the corresponding methyl glycosides. The C_4 shifts for the acetates of the methyl D-fucopyranosides (VII) and (X) and for the free methyl glycosides have different signs. The shifts of the other carbon atoms are close in magnitude. Thus, it may be concluded that the effects of substitution at C_5 in the ^{13} NMR spectra of acetylated methyl glycosides have a longer-range nature.

EXPERIMENTAL

The ^{13}C and ^{1}H NMR spectra were recorded on a Bruker HX-90E instrument. The results, which are given in Table 1 and in Scheme 1, were obtained in $CDCl_3$ relative to TMS.

The methyl glycopyranosides of α- and β-D-xyloses, β-L-arabinose, α-L-rhamnose, α-L-fucose, α- and β-D-glucoses, and α- and β-D-galactoses were obtained by Fischer's method by treating the monosaccharide with methanol in the presence of HCl. Methyl α-L-arabinopyranoside was synthesized by the Koenigs–Knorr method [8]. Methyl β-L-rhamnopyranoside was obtained as described previously [9].

The methyl glycosides were acylated with acetic anhydride in pyridine.

SUMMARY

A comparative discussion of the signals in the ^{13}C NMR spectra of acetylated methyl α- and β-D-xylopyranosides, α- and β-D-glucopyranosides, α- and β-D-galactopyranosides, α- and β-L-arabinopyranosides, α- and β-L-fucopyranosides, and α- and β-L-rhamnopyranosides and of the corresponding free glycosides has shown a similarity of the effects of substitution at C_5 with a longer-range nature of these effects in the case of the acetylated glycosides.

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N-ACYLATED PHOSPHOLIPIDS AND LYSOPHOSPHOLIPIDS OF WILT-RESISTANT VARIETIES OF THE COTTON PLANT

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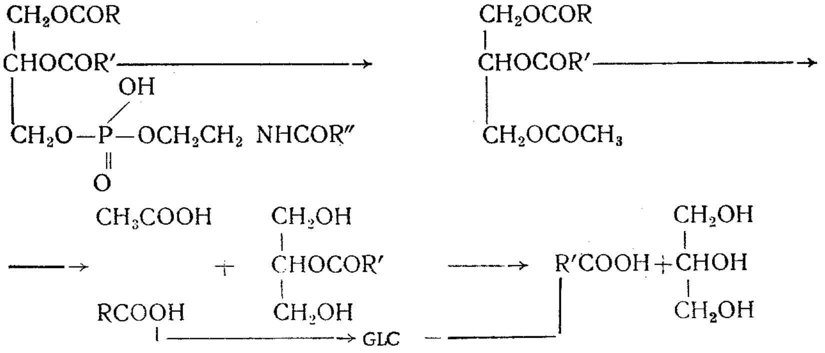
As part of the continuing investigations of the minor phospholipids of the seeds of wilt-resistant varieties of the cotton plant, we have studied the N-acylated phospholipids (N-acylphosphatidylethanolamines and N-acyllysophosphatidylethanolamines) of the varieties Tashkent-1 and Tashkent-3, and also the lysophosphatidylcholines of the varieties Tashkent-1, Tashkent-2, and Tashkent-3. The N-acylated phosphatidylethanolamines were isolated, identified, and analyzed similarly to those from the variety Tashkent-2 [1] by Scheme 1.

The analysis showed the position distributed of the fatty acids in the N-acylphosphatidylethanolamines (Table 1). It follows from Table 1 that the low-molecular-weight $C_{10:0}$ acid, the amount of which in the varieties Tashkent-2 [1] and Tashkent-3 was fairly considerable, was absent from the N-acylphosphatidylethanolamines of the variety Tashkent-1. It is mainly because of this acid that the percentage of low-molecular-weight acids was high in the N-acylphosphatidylethanolamines of the varieties Tashkent-2- and Tashkent-3. The total degree of unsaturation of the molecules of the N-acylphosphatidylethanolamines decreased in the sequence: Tashkent-1 → Tashkent-2 → Tashkent-3. In the N-acylphosphatidylethanolamines of the three varieties of cotton plant, the saturated acids were attached predominantly to the N atom (Table 1).

In the N-acyllysophosphatidylethanolamines, by the methods described previously [1], we established the positions esterified by the fatty acids: as in the case of N-acyllysophosphatidylethanolamines from the variety Tashkent-2, it was position 2 that was substituted in the molecules studied.

In the NMR spectrum there is a multiplet at 5.2 ppm (δ scale) which is characteristic for β-substituted lysophospholipids [2].

The N-acyllysophosphatidylethanolamines of the three varieties had fairly large total unsaturation due to a high content of unsaturated fatty acids in the glycerol moiety of the molecule (O-acyls). Among the fatty acids localized on the N atom there were far more saturated acids than in the corresponding O-acyls. The predominating amount of low-molecular-weight fatty acids ($C_{10:0}$, $C_{12:0}$, $C_{14:0}$) in the N-acylated phospholipids was present in the amide-bound form.



Scheme 1

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