^{13}C NMR SPECTRA OF ACETYLATED HEDERAGENIN GLYCOSIDES

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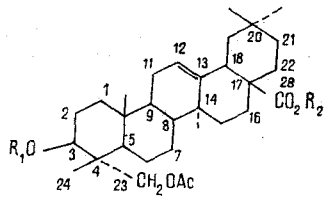
The ^{13}C NMR spectra of acetylated derivatives of the following hederagenin glycosides have been studied hederagenin 3-O-α-L-arabinopyranoside, hederagenin 3-O-[O-α-L-rhamnopyanosyl-(1→2)-α-L-arabinopyranoside], hederagenin 3-O-[O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside], hederagenin 28-O-β-D-glucopyranoside, and hederagenin 28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside]. The spectra give information about the monosaccharide composition, the position of attachment of the carbohydrate chain, and the configurations of the glycosidic bonds, and, in some cases, the orders of the bonds.

^{13}C NMR spectroscopy is widely used in determining the structures of glycosides [1-4], since it is an extremely convenient method because of differences in the regions of the chemical shifts of the overwhelming majority of ^{13}C nuclei of the aglycone and of the carbohydrate moiety. Together with information on the aglycone, ^{13}C NMR spectra permit determination of the configurations of the glycosidic bonds and the position of attachment of the carbohydrate chain to the aglycone and enable information to be obtained on the orders of the bonds and the monosaccharide composition. However, when the spectra are recorded in pyridine or dimethyl sulfoxide, a broadening of the signals of the methine and methylene protons and a superposition of the signals of the solvent are observed. Consequently, in a number of cases it is desirable to study the spectra of acetylated glycosides, which are largely free from these defects.

We have studied the spectra of a number of acetylated hederagenin glycosides (II, IV-VII). In addition to the chemical shifts of the carbohydrate moiety, interest is presented by the mutual influence of the aglycone and a carbohydrate moiety in the C_{28} position, which has not previously been studied.



	R_1	R_2
I.	Ac	H
II.	α-L-Arap 1	H
III.	Ac	CH_3
IV.	α-L-Arap-(1 → 2)-β-D-Glcp	CH_3
V.	α-L-Arap-(1 → 2)- α-L-Rhap	CH_3
VI.	Ac	β-D-Glcp
VII.	Ac	β-D-Glcp-(1 → 6)- β-D-Glcp-(1→4)- α-L-Rhap

The signals in the spectra of compounds (I) and (III) and the aglycones (II, IV-VII) were assigned on the basis of literature information [5-7]. Table 1 gives the chemical shifts of the signals of the carbon atoms of the carbohydrate moiety and some signals of the skeleton in the region of the position of attachment in the carbohydrate moiety.

The chemical shifts of the carbohydrate moiety of (II) coincide with the shifts of methyl α-L-arabinopyranoside acetate [8], with the exception of the C_1 and C_2 shifts. Corresponding differences have been explained by the influence of the aglycone [9]. The assignment of the C_2^{II} and C_5^{II} signals in (IV) was made by selective decoupling from protons, since the H_2, H_3, and H_4 protons, on the one hand, and the H_5 and H_6 protons, on the other, resonate in

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TABLE 1. Chemical Shifts of Some ^{13}C of Acetylated Hederagenin Glycosides

Compound	C_1	C_2	C_3	C_4	C_5	C_{16}	C_{17}	C_{18}	C_{22}	C_{23}	C_{24}	C_{28}
I	37,7	22,95	74,5	40,55	47,8	23,5 (22,95)	46,5	40,9	32,45	65,45	13,1	184,3
II	38,2	25,3	83,0	41,85	47,9	23,6 (22,7)	44,6	41,1	32,05	65,3	12,9	183,9
III	37,8	23,0	74,5	40,55	47,8	23,4 (23,0)	46,7	41,3	32,4	65,4	13,1	178,1
IV	38,1	25,3	84,0	41,8	47,9	23,7 (23,1)	46,8	41,4	32,5	65,4	12,8	178,2
V	38,5	25,8	82,0	42,05	48,0	23,7 (23,1)	46,8	41,45	32,5	65,2	12,8	178,2
VI	37,9	23,0	74,5	40,6	47,9	23,5 (23,0)	46,9	41,1	31,8	65,4	13,1	175,5
VII	37,75	22,95	74,5	40,55	47,8	23,5 (22,95)	46,9	41,1	31,9	65,3	13,1	175,3
	C_1^I	C_2^I	C_3^I	C_4^I	C_5^I	C_6^I	C_1^{II}	C_2^{II}	C_3^{II}	C_4^{II}	C_5^{II}	C_6^{II}
II	102,9	69,6	70,5	67,9	63,2							
IV	103,4	74,9	72,65	68,0[a]	63,0		100,7	71,1	72,8	68,4[a]	71,7	62,1
V	103,65	74,5	71,95	67,85	62,8		98,2	69,7	68,7	71,1	67,2	17,4
VI	91,6	70,1	72,9	68,1	72,5	61,6						
VII	91,6	70,1	72,9	68,5	74,0	67,8	100,5	71,7	74,6[b]	74,4[b]	72,6	61,9
	C_1^{III}	C_2^{III}	C_3^{III}	C_4^{III}	C_5^{III}	C_6^{III}						
VIII	99,35	70,1	68,8	70,7	67,8	17,15						

a,b) Assignment of the signals ambiguous. The values in parentheses are because of the ambiguity of the assignment of the C_{16} and C_{11} signals [5].

different regions [10, 11]. The other signals were assigned on the basis of literature information [8, 10]. However, even after these procedures an indeterminacy remained in the assignment of the C_4^I and C_4^{II} signals. The signals in the spectrum of compound (V) were assigned analogously. The C_3^I, C_5^I, and C_{23} signals in (VI) were assigned by selective decoupling from protons. The assignment of the signals in the spectrum of (VII) was carried out in the following way. The signals of the glucose attached by an ester bond were calculated from (VI) taking into account the contributions of the nonreducing link taken from the ^{13}C NMR spectrum of β-gentiobiose octaacetate [10]. The calculated chemical shifts 91.6, 70.1, 72.9, 68.6, 73.8, and 67.6 ppm for C_1^I, C_2^I, C_3^I, C_4^I, C_5^I, and C_6^I, respectively, practically coincide with the experimental values (Table 1). From the remaining signals, by the method of selective decoupling from protons, it is possible to determine simultaneously the positions of C_6^{II}, C_5^{II}, and C_5^{III}. The signal at 61.9 ppm can be due only to C_6^{II}. The signal at 72.6 ppm is close to the 72.35 ppm calculated for C_5^{II} from the spectrum of β-gentiobiose octaacetate, allowing for the contributions taken from the spectrum of β-maltose octaacetate [10]. The signal at 67.8 ppm (C_5^{III}) is close to the C_5 signal of methyl α-L-rhamnopyranoside acetate [8]. The addition of a monosaccharide unit changes the chemical shift of the α-carbon by a magnitude of +4.5–+8.0 ppm in glucobiose acetates [10]. Consequently, δ for C_4^{II} = 74.4 (74.0) ppm. Similarly, we obtain, as for C_5^{II}: C_2^{II} = 71.7 ppm and C_3^{II} = 74.0 (74.4) ppm. The calculated values are 71.65 and 75.1 ppm, respectively. The chemical shifts of the other signals (70.1, 68.8, and 70.7 ppm) are close to the chemical shifts of the C_2, C_3, and C_4 atoms of methyl α-L-rhamnopyranoside acetate [8] and of the rhamnose in (V).

We have discussed the influence of anomerization on the ^{13}C chemical shifts of acetylated methyl glycosides of monosaccharides previously [8]. The influence of hederagenin on the C_2^I and C_1^I chemical shifts in (II) is similar to the influence of oleanolic acid on methyl β-glucopyranoside acetate [9]. Apparently it is also possible to speak of considerable low-field C_5 shifts of the same sign for nonreducing glucose (from +1.2 to +2.5 ppm [10]) and for nonreducing rhamnose (V, +0.9 ppm, VII, +1.5 ppm) for the α-anomers as compared with the corresponding methyl glycosides. In the case of glucose bound by an ester bond, as in (IV), a weak (about −0.4 ppm) C_2^I shift in comparison with β-D-glucosepentaacetate is observed.

It can be seen from the spectra of compounds (II), (IV), and (V) that a change in the structure of the carbohydrate moiety exerts an influence mainly on the C_1, C_2, and C_3 chemical shifts of the aglycone (Table 1). Since acetylation at C_3 affects the chemical shifts of ring A differently for hederagenin and oleanolic acid, we cannot compare our results with those of Tori et al. [9, 11]; nevertheless, it can be seen that in our case the chemical

shifts mentioned depends on the presence and form of the second monosaccharide. The attachment of a carbohydrate chain by an ester bond causes an upfield shift of C_{28} (about 2.7 ppm).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken on a Bruker HX-90E instrument in $CDCl_3$. The hederagenin glycosides were isolated from *Caulophyllum robustum* Maxim. [12], and they had the following physicochemical properties: hederagenin, mp 318-320°C, $[\alpha]_D^{24}$ +81°; its methyl ester, mp 235-238°C, $[\alpha]_D^{24}$ +68.9°; hederagenin 3-O-α-L-arabinopyranoside, mp 226-228°C, $[\alpha]_D^{24}$ 46.3°; hederagenin 3-O-[O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside], mp 248-250°C, $[\alpha]_D^{24}$ +58.12°; hederagenin 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside], 258-260°C, $[\alpha]_D^{24}$ +12°; hederagenin 28-O-β-D-glucopyranoside, mp 222-225°C, $[\alpha]_D^{24}$ +35°; hederagenin 28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside], $[\alpha]_D^{24}$ −1.8°. Acetylation was carried out with acetic anhydride in pyridine.

SUMMARY

1. The assignment of the signals in the ^{13}C NMR spectra of a number of acetylated hederagenin glycosides has been made and the mutual influence of the aglycone and of the carbohydrate moiety on their chemical shifts has been determined.

2. The results indicate the possibility of interpreting the spectra of the carbohydrate moiety of acetylated glycosides in order to obtain structural information analogous to the information obtained from the spectra of unacetylated glycosides.

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NEW ALKALOIDS OF *Dipthychocarpus strictus*

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New alkaloids with mp 57-59°C and diptamine have been isolated from the seeds and epigeal part of *Dipthychocarpus strictus* collected in Chimkent Province (KazSSR). It has been established that the base with mp 57-59°C has the structure of N,N'-di(6-methylthiohexyl)urea, while diptamine is N-isopropyl-N'-(7-methylsulfonylheptyl)urea.

In a further study of the alkaloids of the seeds of *Dipthychocarpus strictus* [1], a liquid base with bp 193-195°C, deoxodiptocarpaine, diptocarpiline [1-3], and a new alkaloid (I) with mp 57-59°C, composition $C_{15}H_{32}N_2OS_2$, M^+ 320, have been isolated.

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