A STUDY OF SESQUITERPENE LACTONES BY ^{13}C NMR SPECTROSCOPY.

I. ^{13}C NMR SPECTRA OF BADKHYZIN AND ITS DERIVATIVES

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The ^{13}C NMR spectra of badkhyzin and its derivatives have been studied.

The structure of the sesquiterpene lactone badkhyzin has been established previously on the basis of chemical transformations and proton magnetic resonance. It has likewise been shown that badkhyzin, on brief treatment with alkalis, isomerizes, being converted into isobadkhyzin [2].

In the present paper we give the results of a study of badkhyzin and its derivatives by ^{13}C NMR spectroscopy.

In the ^{13}C NMR spectrum of badkhyzin (I) (Fig. 1) and in that of tetrahydrobadkhyzin (II) the signals of all twenty sp^3- and sp^2-hybridized carbon atoms appear, and in their multiplicities correspond completely to the proposed structures (q — quartet, t — triplet; d — doublet; s — singlet):

Compound	Number of groups and multiplicities			
	CH_3—	CH_2—	—CH—	—C—
Badkhyzin (I)	5 q	1 t	7 d	7 s
Tetrahydrobadkhyzin	5 q	3 t	7 d	5 s

The assignment of the signals were made by a comparison with one another of the ^{13}C NMR spectra of (I) and (II) under the conditions of complete and incomplete decoupling (off-resonance) from protons and also by comparison with literature information for the sesquiterpene lactones grosshemin [3], cumambrin A and handelin [4], and others [5].

In the off-resonance spectrum of badkhyzin the quartets of sp^3-hybridized methyl carbon atoms are observed in the strong field region. Of them, the carbon of the methyl group attached to the lactone ring (C-13) resonates at 13.0 ppm. The carbons of the other four methyl groups in the spectrum are found at 15.0, 20.0, 20.5, and 21.0 ppm (C-20, C-18, C-14, and C-15). The fact that the signals at 15.0, 20.0, and 20.5 ppm belong to the C-20, C-18, and C-14 carbon atoms, respectively, is shown by the off-resonance spectra of tetrahydrobadkhyzin in which the C-20 quartet is shifted upfield by 3.5 ppm and that of the C-14 quartet by 4.1 ppm and they are located at 11.5 and 16.4 ppm, respectively, while the C-18 signal in the spectrum of tetrahydrobadkhyzin is shifted downfield by 1.2 ppm. Such behavior of the signal of the methyl group of the badkhyzin side chain can be explained by the cis form of the ester group, i.e., badkhyzin is an angelate of an unsaturated hydroxy keto lactone.

As is well known [6], the signal of a methyl group at a double bond in cis-alkenes shifts downfield on passing to the corresponding alkanes. For example, the chemical shift of the methyl group at the double bond in cis-pent-2-ene (12.3 ppm) increases by 1.2 ppm (downfield shift) in pentane, i.e., it is located at 13.5 ppm; etc. [6]. The signal of the C-15 atom in the spectra of tetrahydrobadkhyzin is found at 21.5 ppm.

The carbon of the only methyl group of the badkhyzin molecule gives a signal in the spectrum at 44.0 ppm.

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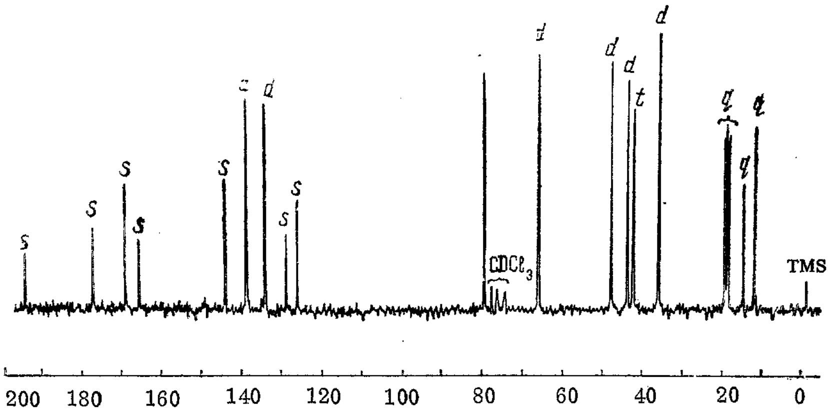


Fig. 1. ^{13}C NMR spectrum of badkhyzin in CDCl$_3$.

As was to be expected, the ^{13}C NMR spectrum of tetrahydrobadkhyzin taken with partial suppression of spin-spin coupling shows three triplet signals (at 26.3, 43.6, and 48.2 ppm), and seven doublets (at 33.5, 36.2, 40.9, 45.2, 50.1, 66.9, and 82.4 ppm) belonging, respectively, to three carbons of methylene groups (C-19, C-9, and C-3) and seven carbons of >CH groups (C-4, C-7, C-17, C-11, C-5, C-8, and C-6). It must be noted that the triplet C-9 and C-3 signals in the spectrum of tetrahydrobadkhyzin, as also the C-9 triplet in the spectrum of badkhyzin, are more descreened with respect to the C-19 signal in (II). The downfield-shift of these signals is due to the descreening influence of the double bond, of the ester group, and of the keto group at C-2, respectively.

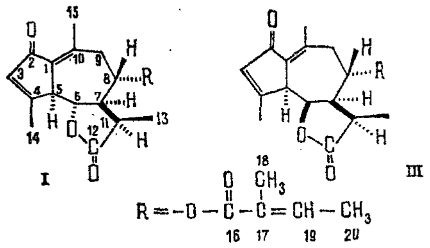
The off-resonance spectrum of badkhyzin has seven doublet signals, five of which belong to five sp^3-hybridized methine carbon atoms (C-5, C-6, C-7, C-8, and C-11), and two to sp^2-hybridized olefinic hydrocarbons (C-3 and C-19).

Doublet signals at 49.0, 67.0, and 81.0 ppm correspond to C-11, C-8, and C-6. The C-5 methine carbon atom resonates at 49.0 ppm. The latter is descreened by 12.5 ppm as compared with the doublet at 37.5 ppm due to C-7. The downfield shift is explained by the presence of double bonds in the α position to it (C-5) [4, 6].

The resonance signals of the olefinic carbon atoms are in the same region as the signals of the carbon atoms of aromatic compounds [6]. The reason for this is the fact that in both classes of compounds these carbon atoms are hybridized in the sp^2 manner. The doublet signals at 135.0 and 140.0 ppm observed in the off-resonance spectrum of (I) belong to the C-19 and C-3 olefinic carbon atoms, respectively. The downfield shift by 5.0 ppm of the C-3 signal as compared with the C-19 signal is caused by the downfield influence of the carbonyl group, which is the α position to C-3.

The singlet signals observed in the spectrum of badkhyzin relate to the seven sp^2-hybridized carbon atoms (C-1, C-2, C-4, C-10, C-12, C-16, and C-17). Of them, two (at 178.2 and 195.5 ppm) belong to the lactonic (C-12) and ketonic (C-2) carbons. The carbon atom of the ester carbonyl group (C-16) gives a signal shifted upfield by 8.2 ppm as compared with the C-12 signal and resonates at 170.0 ppm. This is due to the fact that adjacent to C-16 there is a conjugated double bond which shifts the signal in the upfield direction [6]. A confirmation of this point of view is the paramagnetic shift by 4.2 ppm of the signal of the C-16 atom in the spectrum of tetrahydrobadkhyzin.

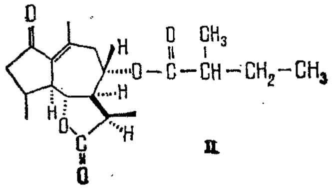
Singlets at 128.0, 130.0, 145.5, and 166.5 ppm relate to the C-4, C-10, C-1, and C-17 atoms, respectively. This assignment was made on the basis of the fact that in the spectrum of tetrahydrobadkhyzin the signals at 128.0 and 166.5 ppm are absent and there are five singlet signals at 205.4 (C-2) and 178.2 (C-12), 174.2 (C-16), 148.3 (C-1), and 131.7 (C-10) ppm.



I

III

$R = -O-\underset{16}{\overset{O}{\overset{\|}{C}}}-\underset{17}{\overset{\overset{18}{CH_3}}{\overset{|}{C}}}=\underset{19}{CH}-\underset{20}{CH_3}$



II

As is well known [6], the introduction of α,β-unsaturation into the α position of a ketone causes a substantial upfield shift of the signal of the carbon atom of the carbonyl group, and therefore in the spectrum of tetrahydrobadkhyzin the signal of the carbon atom of the ketonic group (C-2) is also descreened. The signal is located at 205.4 ppm, and as compared with the analogous signal of badkhyzin it is descreened by 10.1 ppm. This shift is caused by a decrease in the degree of conjugation of the ketone group of tetrahydrobadkhyzin.

Isobadkhyzin (III) differs from badkhyzin stereochemically (at the C-6 center) [7]. The ^{13}C NMR spectrum of isobadkhyzin contains 19 resolved lines, while there are 20 nonequivalent carbon atoms in the molecule. This is the result of the coincidence of the chemical shifts of two ^{13}C nuclei or the result of an incorrect choice of the given parameters in the accumulation of the spectrum. In the off-resonance spectrum of isobadkhyzin there are five quartet, one triplet, five doublet, and six singlet signals (as compared with seven singlets in the spectrum of badkhyzin). A comparison of the ^{13}C NMR spectra of badkhyzin and isobadkhyzin has shown that the change in the stereochemistry of the lactone ring (C-6) leads to a displacement (both upfield and downfield) of the majority of the signals:

Carbon atom	Compound I	 II	 III
1	145.1s	148,3s	143,39s
2	195.15s	205.4s	195.16s
3	140.0d	48.2t	139.65d
4	128.0s	33.5d	126 88s
5	49.0d	50.1d	48,29d
6	81,0d	82,4d	75,96d
7	37.5d	36.2d	40,5d
8	67.0d	66,9d	67.0d
9	44.0t	43.6t	41,08t
10	130.0s	131.7s	129.72s
11	45,0d	45.2d	47.0d
12	178.2s	178.2s	177.1s
13	13.0q	13.1q	10,0 q
14	20,5q	16,3q	16.03q
15	21.0q	21.5q	20.25q
16	170.0s	174.4s	—
17	166.5s	40.9d	166.15s
18	20.0q	21,2q	19.5q
19	135.0d	26.3t	135,14d
20	15.0q	11,4q	15.62q

EXPERIMENTAL

The ^{13}C NMR spectra of the compounds studied were recorded in deuterated chloroform solutions in the pulsed regime with subsequent Fourier transformation under conditions of complete and incomplete decoupling from protons (off-resonance). To reckon the ^{13}C chemical shifts of the substances we used the chemical shift of the central peak of the ^{13}C signal (triplet) of the solvent, which is 76.9 ppm relative to TMS.

The spectrum of compound (I) was taken on a Varian CFT-20 spectrometer, and those of (II) and (III) on a Bruker HX-90 spectrometer.

SUMMARY

The ^{13}C NMR spectra of badkhyzin, tetrahydrobadkhyzin, and isobadkhyzin have been studied. A complete assignment of the signals has been made on the basis of the results of a comparative study of the chemical shifts of the ^{13}C nuclei.

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A STUDY OF SESQUITERPENE LACTONES BY ^{13}C NMR SPECTROSCOPY.

II. ^{13}C NMR SPECTRA OF ALKHANIN, ACETYLARTEMISIN, AND TAUREMISIN

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The ^{13}C NMR spectra of alkhanin, acetylartemisin, and tauremisin have been studied.

The spectra of alkhanin, acetylartemisin, and tauremisin obtained under conditions of complete and partial decoupling (off-resonance) from protons have been investigated. The ^{13}C NMR spectra of these compounds show the signals of all the carbon atoms, corresponding in number of multiplicity to the proposed structures (I), (II), and (III) (q — quartet, t — triplet; d — doublet; s — singlet):

Compound	Number, multiplicity				Hybridized	
	q	t	d	s	sp^3-	sp^2-
Alkanin (I)	3	3	4	5	11	4
Acetylartemisin (II)	4	1	6	6	10	7
Tauremisin (III)	3	2	6	4	11	4

The resonance lines were identified by the comparison with one another of the chemical shifts of the above-mentioned lactones, and also by comparison with literature information [1-4]. The off-resonance spectrum of alkhanin (here and below, in the designation of the multiplicity of a signal, what is presented is the form under the conditions of incomplete decoupling from protons) shows three quartet signals at 12.22, 11.12, and 24.73 ppm, belonging to three sp^3-hybridized carbon atoms (C-13, C-14, and C-15, respectively) [3].

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