

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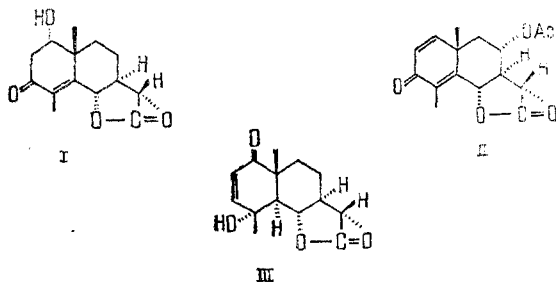
The ^{13}C NMR spectra of alkanin, acetylartemisin, and tauremisin have been studied.

The spectra of alkanin, 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 alkanin (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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As is well known [5, 6], the configurations of the asymmetric centers at C-6, C-7, C-10, and C-11 of alkananin, artemisin, and tauremisin are identical with the configurations of the same atoms of α -santonin, the ^{13}C spectrum of which has been studied [4]. A comparison of the chemical shifts (CS) of the quartet signals of the carbons of the methyl groups attached to the lactone ring in alkananin (12.22 ppm) and in the tauremisin (12.23 ppm) with CS of the CH_3 group at C-11 in α -santonin (12.5 ppm) [4] showed that they differed little, but the signals of the carbon of the CH_3 group at C-11 of acetylartemisin is descreened in comparison with the analogous signals of (I), (III), and α -santonin:

Carbon Atom	Compound		
	I	II	III
1	74.41d	153.12d	201.50s
2	43.30t	125.76d	125.36d
3	200.7s	185.58s	151.59d
4	128.18s	129.42s	69.82s
5	149.43s	148.75s	54.32d
6	81.91d	77.68d	79.33d
7	52.01d	55.98d	52.13d
8	23.97t	69.35d	22.44t
9	33.68t	42.39t	33.96t
10	43.68s	39.75s	46.07s
11	41.66d	40.02d	40.30d
12	177.60s	176.42s	178.08s
13	12.22q	13.62q	12.23q
14	11.12q	10.62q	19.51q
15	24.73q	26.10q	23.52q
16	—	170.00s	—
17	—	20.68q	—

The observed downfield shift is probably caused by the presence of an ester group in the γ position to it (C-8). This shift may also be caused by the cis orientation of the lactone ring in the artemisin molecule, in a similar manner to the shift observed in the transformation of α -santonin into α -episantonin [4]. However, the lactone ring in the artemisin molecule has the trans orientation [6].

One of three triplet signals in the spectrum of alkananin (at 43.30 ppm), unlike the other triplets of CH_2 groups (C-8 and C-9), is shifted downfield. This signal has been assigned to the C-2 carbon atom. Such an interpretation is due to the fact that in the spectra of (II) and (III) not one triplet is descreened as strongly as the C-2 signal in (I). This takes place because of the weak-field influence of both the ketonic and hydroxylic groups present in the vicinal positions to C-2. The signals of the remaining methylene protons of alkananin (C-8 and C-9) appear at 23.97 and 33.68 ppm, respectively. As can be seen from the structure of acetylartemisin, its molecule, unlike those of compounds (I) and (III) and α -santonin, has only one methylene group. The signal of the carbon atom of the latter appears in the spectrum in a somewhat weaker field (at 42.39 ppm) than the analogous signal (C-9) of alkananin, tauremisin, and α -santonin [4]. The downfield shift is due to the vicinal ester function.

The carbon atoms showing doublet signals in the spectra of the lactones under investigation are hybridized in the following manner: in alkananin, all four carbon atoms of CH groups are hybridized in the sp^3 manner, while acetylartemisin and tauremisin each have four sp^3 - and two sp^2 -hybridized carbon atoms. Consequently, in the ^{13}C NMR spectra of compounds (I), (II), and (III) it is possible to isolate two regions with boundaries of 10-82 and

120–205 ppm in which, respectively, the signals from the sp^3 - and sp^2 -hybridized carbon atoms appear.

The doublet signals present in the spectra of compounds (II) (at 125.76 and 153.12 ppm), and (III) (at 125.36 and 151.59 ppm) have been assigned to the olefinic carbons atoms ($CH=CH$). Since alkhaniin does not contain a secondary-secondary double bond, doublet signals are absent from the region of sp^2 -hybridized carbon atoms of the spectrum.

In the region of sp^2 -hybridized carbon atoms in the spectrum of compound (I) there are four singlet signals. Two of them (at 128.18 and 149.43 ppm) belong to the carbons of a tetrasubstituted double bond (C-4 and C-5 respectively), one (at 177.60 ppm) to the carbon of the lactone carbonyl group (C-12), and the last one (at 200.7 ppm) to the ketonic carbon atom (C-3). A comparison of the chemical shifts of the C-4, C-5, and C-12 atoms of compounds (I) and (II) shows that in the main they coincide with those of α -santonin [4]. However, as compared with the analogous signals of (I) and (III), the signal of the carbon atom of the ketone group of (II) (185.58 ppm) is shifted upfield by ~ 15 ppm. The upfield shift takes place under the influence of the conjugated double bonds [7].

EXPERIMENTAL

The ^{13}C NMR spectra of alkhaniin, acetylartemisin, and tauremisin were recorded in deuterated chloroform solutions on a Bruker HX-90 spectrometer under conditions of complete and partial decoupling from protons (off-resonance). To reckon the magnitudes of 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.

SUMMARY

1. The ^{13}C NMR spectra of alkhaniin, acetylartemisin, and tauremisin have been studied.
2. A complete assignment of the resonance lines of the spectra 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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