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

III. ^{13}C NMR SPECTRA OF ARTEMIN AND ITS DERIVATIVES

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The ^{13}C NMR spectra obtained under conditions of complete and incomplete decoupling from protons of the sesquiterpene lactone artemin (I), its dihydro derivative (II), and its acetyl derivative (III) have been studied. An assignment has been made of the chemical shifts of all the carbon atoms by comparison of the ^{13}C NMR spectra of (I), (II), and (III) with one another and also by comparison with literature information.

The ^{13}C NMR spectra of sesquiterpene lactones belonging to two groups — guaianolides and eudesmanolides with conjugated systems — have been considered previously. We now give the results of the investigations of the ^{13}C NMR spectra of hydroxy-containing eudesmanolides — artemin (I), dihydroartemin (II), and acetylartemin (III). The spectra of these compounds show the signals of all the carbon atoms, and these signals correspond in hybridization and multiplicity to the proposed structures.

The spectra were interpreted by comparing the ^{13}C NMR spectra of (I), (II), and (III) obtained under the conditions of complete and incomplete (off-resonance) decoupling from protons, taking literature information [2, 3] into account.

In the spectra of (I), (II), and (III) it is possible to isolate a region of signals of sp^3-hybridized atoms (12-81 ppm) and a region of sp^2-hybridized carbon atoms (82-180 ppm).

The carbon atom bearing the secondary hydroxy group, C_1, and that bearing the tertiary hydroxy group, C_5, of artemin are revealed in the off-resonance spectrum of (I) in the form of a doublet (at 71.66 ppm) and a singlet (at 76.8 ppm), respectively. The latter of these signals appears in the spectra of artemin and its acetate in the region of the central peak of the triplet from the solvent — $CDCl_3$. On passing to the dihydro derivative (II), as was to be expected, the singlet signal of the C_5 carbon atom shifts upfield by 1.62 ppm (Table 1). The introduction of an acetyl group into the molecule of (I) ((I) monoacetate) leads to a paramagnetic shift (by 2.91 ppm) of the C_1 doublet.

The methylene carbon atoms of artemin are represented by four triplets at 30.28, 29.84, 29.60, and 22.75 ppm. Since an OH group possesses a definite weak-field influence [4] on a vicinal methylene group, the signal at 30.28 ppm is assigned to the C_2 carbon. We assigned the signal at 22.75 ppm to the C_8 carbon. Of the remaining two triplets signals of methylene groups, that at 29.84 ppm belongs to the C_9 carbon. The descreening of the latter by 0.24 ppm as compared with the signal of the C_3 carbon (29.60 ppm) takes place because of the β-influence of the methyl group at C_{10}.

On comparing the chemical shifts (CSs) of the carbons of the methylene groups of (I), (II), and (III), it can be seen that, with the exception of the triplet at 26.82 ppm in (III), all the CSs agree well. The triplet at 26.82 ppm in the off-resonance spectrum of acetylartemi has been assigned to the carbon of the C_2 methylene group. The diamagnetic shift of this signal as compared with those of the analogous carbon atoms in (I) and (II), is caused by the presence of the acetyl group, which makes a smaller β-contribution than the hydroxy group [2, 4].

In the region of sp^3-hybridized carbon atoms in the spectrum of artemin there are also two quartet signals belonging to the carbons of two methyl groups. The quartet at 12.37 ppm corresponds in its value to the carbon of the methyl group at C_{13} of the lactone ring with a trans-linked lactone ring [5]. The correctness of the assignment of the signal at 12.37 ppm

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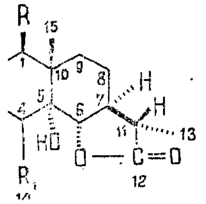
TABLE 1

Carbon atom	Chemical shifts, ppm		
	I	II	III
C_1	71,66d	71,82d	74,57d
2	30,28t	30,65t	26,82t
3	29,60t	29,20t	29,28t
4	145,02s	33,43d	144,54s
5	76,80s	75,10s	76,80s
6	81,74d	85,06d	81,31d
7	41,17d	40,82d	41,11d
8	22,75t	22,75t	22,60t
9	29,84t	29,68t	29,78t
10	44,52s	44,73s	43,77s
11	45,37d	45,94d	45,17d
12	179,29s	179,29s	179,09s
13	12,37q	12,35q	12,36q
14	112,27t	16,69q	112,62t
15	13,18q	13,48q	14,45q
16	—	—	170,30s
17	—	—	21,12q

to C_{13} is confirmed by the CS of the quartet signal in (II) and (III) (see Table 1). As can be seen from Table 1, the CSs of the C_{13} signal in the spectra of (II) (12.35 ppm) and (III) (12.36 ppm) remain unchanged.

The lactone carbon atom C_6 in the spectrum appears in the form of a doublet at 81.74 ppm. The CS of the signal under discussion is characteristic for a trans-orientated lactone ring [5]. It must be mentioned that, according to available information, the CS of a lactone carbon atom depends on the orientation of the lactone ring in the molecule. With the trans orientation, the signal of the lactone carbon is found in a weaker field ($\sim$4-5 ppm) than with the cis orientation. For example, the signal of the lactone carbon atoms in α- and β-santonins shift upfield on their conversion into the corresponding α- and β-episantonins [5]. This signal in the ^{13}C NMR spectra of badkhysin behaves similarly in the transition to the epi derivative (isobadkhysin) [1].

The off-resonance spectrum of artemin has four singlet signals, two of which belong to two sp^3-hybridized carbon atoms (C_5 and C_{10}) and two to sp^3-hybridized carbon atoms (C_4 and C_{12}). The signal at 44.52 ppm is assigned to C_{10}. This signal in the spectrum of the acetyl derivative (III) appears with an upfield shift of 0.75 ppm. In contrast to this, the quartet of the methyl group at C_{10} in the spectrum of (III) is shifted downfield by 1.27 ppm in comparison with that in the spectrum of (I). The diamagnetic shift of the C_{10} signal and the paramagnetic shift of the quartet of the methyl group at C_{10} can be explained by the presence of an acetyl group in the molecule of (III)



I. $R = -OH$; $R_1 = -CH_2$

II. $R = -OH$; $R_1 = -CH_3$

III. $R = -OCOCH_3$; $R_1 = =CH_2$

The remaining singlet signals, corresponding to C_4 and C_{12} in the spectrum (I) are located at 142.02 and 179.29 ppm.

The signal of the exomethylene group at C_4 (C_{14}) in the off-resonance spectrum of artemin was detected in the form of a triplet at 112.27 ppm. The fact that this belongs to C_{14} was shown by the hydrogenation of (I). In the spectrum of (II), the C_{14} atom gave a quartet signal at 16.69 ppm.

EXPERIMENTAL

The ^{13}C NMR spectra of artemin, dihydroartemin, and acetylartemin were recorded in deuterated chloroform solutions on a Bruker HX-90 spectrometer under conditions of complete and incomplete (off-resonance) decoupling from protons. To calculate the values of the ^{13}C

chemical shifts of the substances we used the chemical shift of the central peak of the ^{13}C triplet of the solvent, equal to 76.9 ppm relative to TMS taken as zero.

SUMMARY

The ^{13}C NMR spectra of artemin, dihydroartemin, and acetylartemin have been studied, and an assignment of the signals has been made on the basis of a comparative analysis of the chemical shifts of the ^{13}C nuclei.

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ARTAPSHIN — A NEW SESQUITERPENE LACTONE FROM *Artemisia fragrans*

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A new sesquiterpene lactone, $C_{15}H_{22}O_4$, which has been called artapshin (I) has been isolated from *Artemisia fragrans* Willd. The acetylation of (I) led to its diacetate $C_{19}H_{26}O_6$, mp 160-162°C (II). The saponification of (II) gave a dihydroxylactone $C_{15}H_{22}O_4$, mp 118-120°C. A structure has been proposed from artapshin on the basis of its chemical and spectral (IR and NMR) characteristics.

A substance with the composition $C_{15}H_{22}O_4$, which has not been possible to crystallize, has been isolated by chromatography on a column of alumina from the resin obtained by extracting the epigeal part of *Artemisia fragrans* Willd. (fragrant wormwood) gathered on the Apsheron peninsular in August, 1981.

The IR spectrum of the compounds has bands of OH groups (3420 cm^{-1}), of a γ-lactone ring (1760 cm^{-1}) and of a double bond (1670 cm^{-1}). The presence in the spectrum of strong bands at 910 and 970 cm^{-1} permits the conclusion that the molecule of the lactone contains an exomethylene group. Acetylation of the compound led to a diacetate with the composition $C_{19}H_{26}O_6$, mp 160-162°C (chloroform—hexane). The IR spectrum of the diacetate had maxima at (cm^{-1}), 1780 (C=O of a γ-lactone); 1740, 1250, 1240 (C=O of acetyl groups); and 1660, 970, 900 (exocyclic methylene groups). The saponification of the diacetyl derivative gave a dihydroxylactone, $C_{15}H_{22}O_4$, mp 118-120°C (chloroform—hexane). The IR spectrum of the latter showed the bands of OH groups (3200-3360 cm^{-1}), of the CO group of a γ-lactone ring (1780 cm^{-1}), and of a double bond (1660, 990, 967, 900, 890 cm^{-1}).

Judging from the NMR spectrum of the acetyl derivative (Fig. 1), the lactone under investigation was based on a eudesmane carbon skeleton. This is indicated by the following features revealed by the spectrum: a singlet (at 0.97 ppm, 3H, $CH_3-\overset{|}{\underset{|}{C}}-$) of an angular methyl group, and a triplet (at 4.12 ppm, $J_1 = J_2 = 11$ Hz, 1 H) of a lactone proton, the ratio of

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