A STUDY OF BADKHYZININ

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The treatment of badkhyzinin with a mixture of fuming hydrochloric and glacial acetic acids has yielded a substance with the composition $C_{20}H_{25}O_5Cl$, mp 169-171°C (decomp.). Its IR spectrum in the region of characteristic frequencies has bands at (cm^{-1}) 3480 (OH group), 1770 (CO of a γ-lactone ring), 1705 and 1270 (CO of an α,β-unsaturated ester group), and 1650 (double bonds).

Acetylation of the chlorohydrin led to the formation of a monoacetate with the composition $C_{22}H_{27}O_6Cl$, mp 132-133°C. The IR spectrum of the latter showed the bands of a CO group of a γ-lactone ring (1780 cm^{-1}), of the CO group of an α,β-unsaturated ester (1725, 1260 cm^{-1}), of the CO of an acetyl group (1750, 1240 cm^{-1}), and of double bonds (1650 cm^{-1}). The spectrum lacked the maximum of an OH group.

The NMR spectrum of the chlorohydrin (Fig. 1) showed the singlet of an angular methyl group at 1.02 ppm (3 H, $CH_3-\overset{|}{\underset{|}{C}}-$), a triplet at 1.96 ppm (J = 2 Hz, 3 H, $CH_3-\overset{|}{C}=$) and a doublet (each component of which consisted of a triplet) with its center at 2.08 ppm (J_1 = 7 Hz, J_2 = 2 Hz, 3 H, $CH_3-CH=$), showing the presence of an angelicyl group in the molecule of the compound.

We may note that in the NMR spectrum of badkhyzinin taken in deuterated chloroform solution the protons attached to the oxide ring (H-2 and H-3) are found in the form of a two-proton doublet at 3.76 ppm. Only recording the spectrum in benzene solution enabled the structure of the signals to be resolved [1]. Now the shift between the signals of these protons was 0.18 ppm, while the shift between the H-2 and H-3 signals in the NMR spectrum of the chlorohydrin was 0.56 ppm. The spin–spin coupling constant of the protons attached to the oxide ring of badkhyzinin is 3 Hz. This shows the α orientation of the oxide ring (see partial structure A) [2].

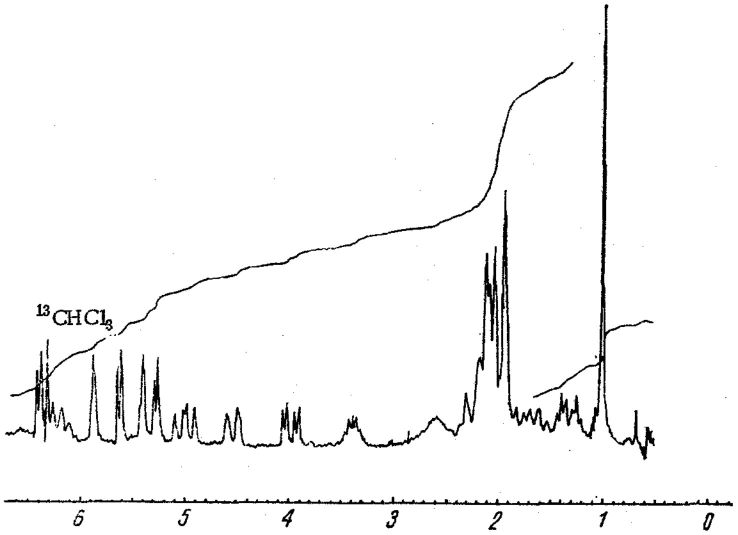

Fig. 1. NMR spectrum of the chlorohydrin of badkhyzinin.

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TABLE 1.

Compound	Solvent	CH_3 at C-10	CH_3 of ester groups	—CH— of ester groups	Protons attached to C							
					1	2	3	5	6	7	13	14
Badkhyzinin chlorohydrin (mp 169-171°C)	$CHCl_3$	1,02 s	1,96 t J = 2 Hz 2,08 d/t J = 7 Hz J = 2 Hz	6,22 m J = 7 Hz J = 2 Hz	5,28 d J = 3 Hz	3,98 q J = 10 Hz J = 3 Hz	4,54 d/t J = 10 Hz J = 2 Hz	2,25 J = 10 Hz	5,0 q J = 10 Hz J = 8 Hz	3,39 m	5,63 d J = 4 Hz 6,39 d J = 4 Hz	5,4 t J = 2 Hz 5,88t J = 2 Hz

Note. s) singlet; d) doublet; t) triplet; q) quartet; m) multiplet; d/t) doublet each component of which consists of a triplet.

Since the —I effect of chlorine is greater than the +C effect [3], the shell of valence electrons from the remaining part of the molecule is repelled toward the chlorine atom. This also apparently explains the paramagnetic shift of the signals of the protons of ring A (see Table 1), i.e., the protons at C-1, C-2, C-3, and C-14 of the chlorohydrin molecule as compared with those of badkhyzinin.

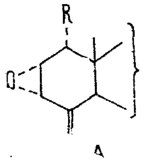
The protons at C-2 and C-3 in the NMR spectrum of the chlorohydrin appear in the form of a quartet at 3.98 ppm (J_1 = 10 Hz, J_2 = 3 Hz) and of a doublet with its center at 4.54 ppm (J = 10 Hz), each component of the doublet being split additionally into a triplet with a spin—spin coupling constant of 2 Hz, probably because of allyl interaction with the protons of the exomethylene group at C-14.

The most considerable downfield shift, by 0.78 ppm, is undergone by the H-3 atom of the chlorohydrin as compared with the chemical shift of the analogous proton of badkhyzinin [1]. The shift between the signals of the protons of the exomethylene group at C-4 of the chlorohydrin is also large, amounting to 0.48 ppm, while the shift between the signals of the same protons of badkhyzinin is 0.18, of badkhyzidin 0.15 [4], of the hydroxylactone 0.10 [5], and of erevanin 0.18 [6]. All these facts show the addition of the chlorine to C-3.

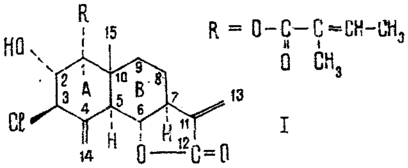
A comparison of the spin—spin coupling constants of the protons at C-5, C-6, and C-7 of badkhyzinin [1] and the chlorohydrin show that they are in the trans position to one another. So far as concerns the configuration of the OH group and of the chlorine atom, as is known [2], the addition of HCl to α-oxides takes place in the trans position and the opening of an oxide ring leads predominantly to the inversion of the configuration at that carbon atom the bond of which with oxygen is broken during the reaction.

On the other hand, the similarity of the UV spectra of compounds containing an α-oxide ring and a double bond in the adjacent positions or a C=O group has been established. The addition of HCl to an ethylenic double bond takes place not in the manner of an ordinary diaxial addition but with the formation of more stable compounds — β-chloro derivatives [7].

If we take into account the equatorial addition of chlorine, on the one hand, and the spin—spin coupling constants between the protons at C-1, C-2, and C-3 (3 and 10 Hz, respectively), structure I is the more probable for badkhyzinin chlorohydrin:



A



$R = O-\underset{\underset{O}{\parallel}}{C}-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$

I

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument in paraffin oil and the NMR spectrum on a Varian HA 100 spectrometer in chloroform solution with TMS as internal standard, the chemical shifts being given on the δ scale. The results of the elementary analyses of the compounds corresponded to the calculated figures.

Preparation of the Chlorohydrin. A solution of 0.5 g of badkhyzinin in 5 ml of glacial acetic acid was treated with 5 ml of fuming hydrochloric acid. After heating on the water bath for 5 min the mixture was left at room temperature for 24 h and was diluted with water and extracted with chloroform. The chloroform extracts were washed with water, dried over Na_2SO_4, and filtered, and the chloroform was distilled off. On standing, a solution of the residue in a mixture of diethyl ether and petroleum ether deposited a crystalline substance which, after recrystallization from the same mixture of solvents, had mp 169-171°C (decomp.). Yield 75%.

Acetylation of the Chlorohydrin. A solution of 0.03 g of badkhyzinin chlorohydrin in 0.3 ml of pyridine was treated with 0.3 ml of acetic anhydride, and the mixture was heated on the water bath (for 1 min) and was left at room temperature for 24 h. Then it was evaporated in a porcelain dish on the water bath, the residue was dissolved in diethyl ether, and the solution was filtered through a 1 cm layer (*d* 1 cm) of deactivated Al_2O_3. Crystals of $C_{22}H_{27}O_6Cl$ with mp 132-133°C were obtained from a mixture of ether and hexane. Yield 95%.

SUMMARY

It has been established that in the formation of the chlorohydrin, the opening of the oxide ring of badkhyzinin takes place mainly from the side of the methylenic double bond.

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THE STRUCTURES OF JUNIFERIN AND JUNIFERININ

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We have previously reported the isolation from the roots of *Ferul juniperina* Eug. Kor. of the new substances juniferin (I) and juniferinin (II), which are esters of the sesquiterpene alcohol juniferol with vanillic (I) and p-hydroxybenzoic and acetic (II) acids, respectively [1].

In the present paper we give a proof of the structures of these substances. Since juniferin (I) and juniferinin (II) are esters of juniferol (III), the determination of the structures of (I) and (II) amounted to the elucidation of the structure of (III) and a determination of the positions of the acyl residues in the esters.

Juniferol (III), with the composition $C_{15}H_{26}O_2$ (M^+ 238), gives an IR spectrum having absorption bands at 1665 cm^{-1} (double bond) and 3200-3600 cm^{-1} (hydroxy group), and a UV spectrum with a maximum at 211 nm (log ε 3.2), which is characteristic for a nonconjugated double bond. The presence in the PMR spectrum of (III) (Fig. 1a) of the signals from two olefinic and two vinylmethyl protons shows that juniferol contains two double bonds.

The composition, the presence of two double bonds, and the absence of carbonyl and epoxy groups, and also the nature of the signals of the methyl groups in the PMR spectrum of (III) permit the assumption that the monocylic skeleton of humulane (X) is the most probable for juniferol [2-6]. The positions of the hydroxy groups and of the double bonds were established on the basis of the following chemical transformations and spectral characteristics. Since

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