STEREOCHEMISTRY OF THE EUDESMANOLIDES OF *Ferula oopoda*

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The configurations of badkhyzinin, badkhyzidin, a hydroxylactone, oopodin, dehydrooopodin, and feropodin are considered on the basis of the results of PMR spectroscopy.

Determination of the structures of the eudesmanolides badkhyzinin [1], badkhyzidin [2], oopodin and dehydrooopodin [3], a hydroxylactone [4], and feropodin [5], isolated from the resin of the roots of *Ferula oopoda* (Boiss. et Buhse.) Boiss. have been reported previously. In the present paper we give the results of an investigation of the stereochemistries of the eudesmanolides mentioned.

In the badkhyzinin (i) molecule, the oxide ring apparently has the α-orientation. This is indicated by the spin–spin coupling constants (SSCCs) of the protons of the oxide ring in the NMR spectrum recorded in benzene: H-3, doublet, δ 3.25 ppm, $J = 3$ Hz; and H-2, quartet, δ 3.43 ppm, $J_1 = 5$ Hz, $J_2 = 3$ Hz. The signals of these protons coincide in the spectra of badkhyzinin and badkhyzidin (II) taken in $CdCl_3$ [1, 2], and therefore it is impossible to consider the structure of the H-2 and H-3 signals separately. Only recording the spectrum in benzene makes it possible to determine the multiplicity and SSCCs. It must also be mentioned that the signals of the protons at the C-1 ester groups in the NMR spectra of badkhyzinin and badkhyzidin taken in $CDCl_3$ appear in the form of multiplets. The signals of the vinylmethyl groups and of the vinyl proton of the ester group and of the exocyclic methylene at C-4 and of the proton at C-5 are also subjected to additional splitting, which apparently results from the long-range spin–spin coupling of the protons [1].

In the NMR spectra taken in benzene, the signal of the proton at C-1 is observed in the form of a doublet at 4.49 ppm with a SSCC of 5 Hz, which shows the α-orientation of the ester group in the molecule of both badkhyzinin and badkhyzidin.

The orientation of the angular methyl group in (I) is probably the same as that of the $CH_3-\overset{|}{\underset{|}{C}}-$ group in erivanin [6], alkhanin, alkhanol [7], and others. This conclusion is based on the fact that the signal of this group in the NMR spectrum of badkhyzinin taken in benzene is shifted upfield (in comparison with the spectrum taken in deuterated chloroform) by the same amount as the signal of the $CH_3-\overset{|}{\underset{|}{C}}-$ group of the lactones compared (ppm);

Compound	$CDCl_3$	C_6H_6	$\Delta\delta = \delta_{CDCl_3} - \delta_{C_6H_6}$
Badkhyzinin	0.84	0.40	0.44
Badkhyzidin	0.86	0.42	0.44
Erivanin diacetate	0.91	0.51	0.40
Alkhanol diacetate	1.16	0.76	0.40

The results of a consideration of the SSCCs of the protons at C-5, C-6, and C-7 of badkhyzinin show their trans arrangement in relation to one another [1]. A similar arrangement of H-5, H-6, and H-7 is also characteristic for badkhyzidin, oopodin, dehydrooopodin, the hydroxylactone, and feropodin [2-5].

As pointed out previously [2], the sodium tetrahydroborate reduction of badkhyzinin forms a dihydro derivative identical with a natural eudesmanolide – badkhyzidin, and the saponification of the latter leads to deangelicylbadkhyzidin, which has been identified as the hydroxyl-

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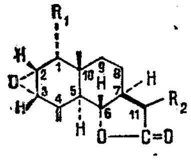
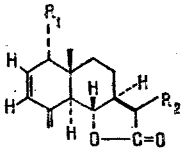
actone (III) and has been isolated from the roots of *F. oopoda*. This indicates the similar configurations of the substituents of badkhyzinin, badkhyzidin, and the hydroxylactone at C-1, C-2, C-3, C-5, C-6, and C-7. The SSCCs of the protons at C-1 (6 Hz), C-5 (10 Hz), C-6 (10 and 7.5 Hz), and C-7 with the protons in the vicinal positions in the NMR spectra of oopodin (IV) and of dehydro-oopodin (V), and the diamagnetic shift by 0.43 ppm of the singlet of the angular methyl group in the spectra taken in benzene (as compared with the spectra in deuterated chloroform) permit the conclusion that the spatial positions of the substituents at C-1, C-5, C-6, C-7, and C-10 of the latter are the same as for the corresponding asymmetric centers of badkhyzinin.

It is known [8, 9] that the diamagnetic shift due to an aromatic solvent (benzene) of the doublet of an α-methyl group at a lactone ring in eudesmanolides amounts to 0.23 ± 0.06 ppm, while the signal of a β-oriented CH_3 group shifts by 0.46 ± 0.06 ppm. To determine the orientation of the methyl group at C-11, the NMR spectra of badkhyzinin and of oopodin were taken in $CDCl_3$ and C_6H_6. The shift of the signal of the protons of this group caused by the aromatic solvent was found to be 0.26 ppm for badkhyzidin and 0.27 ppm for oopodin. The values of the shifts of the signals of the CH_3 groups at C-11 of the latter permit the assumption that the methyl at C-11 in the molecules both of badkhzydin and of oopodin have the α-orientation.

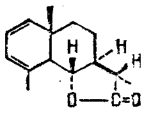
The facts given indicate the biogenetic relationship of the eudesmanolides present in the resin of the roots of *F. oopoda*. Consequently, it may be assumed that the methyl groups at C-10 and C-11 in the feropodin (VI) molecule have the same orientation as the corresponding CH_3 groups in badkhyzidin, oopodin, and the hydroxylactone. This point of view is confirmed by the NMR spectrum of feropodin taken in benzene solution. In it the signals of the angular methyl group ($CH_3\!-\!\overset{|}{\underset{|}{C}}\!-$ at C-10) and of the secondary methyl $\left(CH_3\!-\!CH\!\langle\right.$ at C11) shift in the upfield direction by 0.39 and 0.24 ppm, respectively.



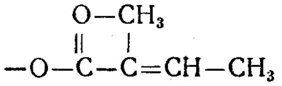
I,II,III



IV,V



VI



$$\text{I, II, IV, V. } R_1- \quad -O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3$$

$$\text{III. } R_1= \quad -OH$$

$$\text{I, V. } R_2=CH_2$$

$$\text{II, III, IV. } R_2- \quad -CH_3$$

EXPERIMENTAL

The NMR spectra were taken on a Varian HA-100D spectrometer in solutions in deuterated chloroform and in benzene. Tetramethylsilane was used as internal standard. The chemical shifts are given in the δ scale.

SUMMARY

The configuration of badkhyzinin, badkhyzidin, a hydroxylactone isolated from *F. oopoda*, oopodin, dehydrooopodin, and feropodin have been considered on the basis of the results of NMR spectroscopy.

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