

BADKHYSIDIN - A NEW SESQUITERPENE LACTONE
FROM THE ROOTS OF *Ferula oopoda*

S. V. Serkerov

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Continuing an investigation of the resin of the roots of *Ferula oopoda* (Boiss, et Buhse) Boiss, we have isolated a substance with the composition $C_{20}H_{26}O_5$, mp 117-118°C. From its elementary composition and IR spectrum, it can be assigned to the sesquiterpene lactones containing an ester grouping. When the physicochemical properties of the compound isolated were compared with those of known sesquiterpene lactones, it was seen that it is a new substance, and the name badkhysidin has been proposed for it.

The IR spectrum of badkhysidin shows the bands of a γ -lactone (1770 cm^{-1}), an α, β -unsaturated ester (1710 cm^{-1}), and of double bonds (1650 cm^{-1}). The presence of a lactone ring is confirmed by the fact that the substance is soluble in alkaline solutions on heating. The presence of an ester group in it and its nature are shown by the saponification of badkhysidin. This gives a substance $C_{15}H_{20}O_4$, mp 212-214°C, and tiglic acid, identified from its IR spectrum.

The IR spectrum of the saponified product shows the maxima of an OH group (3540 cm^{-1}), a γ -lactone ring (1760 cm^{-1}), and a double bond (1650 cm^{-1}). The results of a comparison of the melting points and the IR and NMR spectra of saponified badkhysidin and a recently isolated hydroxylactone [1] showed that they are identical. A mixture of the samples being compared gave no depression of the melting point.

Thus, of the five oxygen atoms present in the molecule of badkhysidin, two participate in the formation of the lactone ring, two in an ester group, and the fifth is apparently present in the form of an epoxy group.

On the basis of these facts, it may be assumed that badkhysidin, like feropodin [2], badkhysin [3], and others, belongs to the sesquiterpene lactones of the eudesmane series.

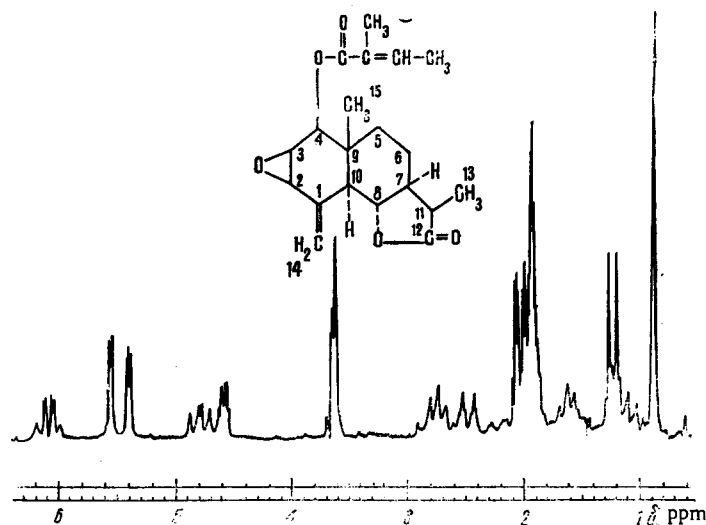


Fig. 1. NMR spectrum of badkhysidin.

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TABLE 1. NMR Spectra of Badkhsinin and Badkhsidin

Compound	CH ₃ at C ₉	CH ₃ of ester group	-CH= of ester group	CH ₃ at C ₁₁	Protons at C							
					2	3	4	7	8	10	13	14
Badkhsinin	s* 0,81	t 1,85 d/t 1,95 J=7 Hz	m 6,15	—	d 3,65 J=2 Hz	d 3,65 J=2 Hz	m 4,65	m 3,27	q 4,87 J ₁ =10 Hz J ₂ =7,5 Hz	d/t 2,25 J=10 Hz	d 6,29 J=4 Hz d 5,54 J=1 Hz	d 5,47 J=2 Hz d 5,59 J=2 Hz
Badkhsidin	s 0,83	t 1,92 d/t 2,01 J=7 Hz	m 6,08	d 1,23 J=6 Hz	t 3,64	t 3,61	m 4,58	—	q 4,80 J ₁ =10 Hz J ₂ =7,5 Hz	d/t 2,48 J=10 Hz	—	d 5,40 J=2 Hz 5,55 J=2 Hz

* s singlet; d doublet; t triplet; q quartet; m multiplet; d/t doublet, each component of which is split into a triplet.

The NMR spectrum of badkhsidin (Fig. 1 shows the presence of an angular methyl group (singlet at 0.88 ppm, $\text{CH}_3-\text{C}-$), a secondary methyl group (doublet at 1.23 ppm $\text{CH}_3-\text{CH}<$, J=

6 Hz), a vinylmethyl ester group (triplet at 1.92 ppm, $\text{CH}_3-\text{C}=\text{C}$), a doublet each component of which consists of a triplet, 2.04 ppm, $\text{CH}_3-\text{CH}=\text{C}$, J=7 Hz), an olefinic proton of an ester (multiplet at 6.08 ppm, $-\text{CH}=\text{C}$), protons at an epoxy group (triplet at 3.64 ppm, J=2 Hz), protons at an ester group (multiplet at 4.58 ppm), of a lactone ring (quartet at 4.80 ppm, J₁=10 Hz, J₂=7.5 Hz) and of an exocyclic methylene group (doublets at 5.40 and 5.55 ppm, J=2 Hz, $\text{CH}_2=\text{C}<$). On comparing the NMR spectra of badkhsinin and badkhsidin, their similarity can be seen (Table 1). Consequently, assuming the possibility of obtaining badkhsidin from badkhsinin by the saturation of one double bond of the latter, we hydrogenated it. However, it was impossible to isolate badkhsidin from the mixture obtained. Only the reduction of badkhsinin with sodium tetrahydroborate in methanolic solution led to the dihydro derivative badkhsidin (mp 117–118°C). The IR and NMR spectra of dihydrobadkhsinin and of badkhsidin were identical. A mixture of the two compounds gave no depression of the melting point.

It has been established that badkhsinin contains three double bonds. Consequently, it was necessary to determine which double bond was reduced in the formation of badkhsidin.

The presence in the NMR spectrum of the compound under investigation of the signals of two vinylmethyl groups and an olefinic proton shows that there is a double bond in the side chain of the molecule. Furthermore, the spectrum has two doublets (5.40 and 5.55 ppm) due to an exocyclic methylene group. Each signal is split by 2 Hz. Usually, an exocyclic methylene group on a lactone ring forms two doublets with spin-spin coupling constants of not less than 3 Hz [3–9]. Consequently, it may be considered that badkhsidin is the product of the reduction of the methylene double bond at the lactone ring.

This hypothesis is confirmed by the nature of the splitting of the one-proton signal at 2.48 ppm. This signal, as in the NMR spectrum of badkhsinin [3], consists of a doublet (because of coupling with the neighboring proton at C₈) with a constant of 10 Hz. Apart from this, each component of the signal is split additionally into a triplet. This probably takes place as the result of allyl interaction of this proton (H-10) with the $>\text{C}=\text{CH}_2$ group at C₁.

The absence of a multiplet signal at 3.27 ppm in the NMR spectrum of badkhsinin permits the assumption that badkhsidin is the 11,13-dihydro derivative of badkhsinin (I).

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer (paraffin oil), and the NMR spectra on a Varian HA-100D instrument (solution in deuterated chloroform). The internal standard was tetramethylsilane, and the chemical shifts are given on the δ scale.

Preparation of Badkhysidin. The mother solutions from the recrystallization of badkhysinin obtained by a known method [10] were combined, part of the ethanol was evaporated off, and the residue was left at room temperature. The solution was separated from the crystals that deposited. The crystals were filtered off and repeatedly recrystallized from aqueous ethanol; mp 117–118°C. Found %: C 69.51; 69.42; H 7.70; 7.62. $C_{20}H_{26}O_5$. Calculated %: C 69.34; H 7.57.

Saponification of Badkhysidin. A solution of 0.2 g of badkhysidin in 15 ml of methanol was treated with 10 ml of 5% KOH. The mixture was heated in the water bath for 30–40 min, diluted with water, cooled, and acidified with dilute H_2SO_4 . Then it was extracted with diethyl ether. The ethereal extract was washed with water and shaken with 0.5% sodium carbonate solution. The organic layer was separated off, dried with Na_2SO_4 , filtered, distilled to small volume, and treated with petroleum ether. The crystals that deposited were recrystallized from aqueous ethanol; mp 212–214°C. Found %: C 68.20; 68.41; H 7.90; 7.85. $C_{15}H_{20}O_4$. Calculated %: C 68.16; H 7.63.

The sodium carbonate layer was acidified and was shaken with diethyl ether. The ethereal extract was dried with Na_2SO_4 , filtered, and distilled. The residue consisted of a crystallizing oil, the IR spectrum of which coincided completely with that of tiglic acid.

Reduction of Badkhysinin with $NaBH_4$. A solution of 0.5 g of badkhysinin in 30 ml of methanol was treated with 1.0 g of sodium tetrahydroborate in methanol. The mixture was left at room temperature for 10 min, diluted with water, acidified with 20% H_2SO_4 , and extracted with diethyl ether. The ethereal layer was separated off, washed with water three times, and dried with Na_2SO_4 . Then it was filtered and distilled. The residue, a viscous oil, was dissolved in a mixture of diethyl ether and petroleum ether. The crystals that deposited were filtered off and recrystallized from aqueous ethanol; mp 117–118°C.

SUMMARY

1. A new sesquiterpene lactone with the composition $C_{20}H_{26}O_5$, mp 117–118°C, which has been named badkhysidin, has been isolated from the resin of the roots of Ferula oopoda (Boiss. et Buhse) Boiss.
2. It has been established that badkhysidin has the structure of 11,13-dihydrobadkhysinin.

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