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FEROPODIN—A SESQUITERPENE LACTONE FROM THE ROOTS OF *FERULA OOPODA*

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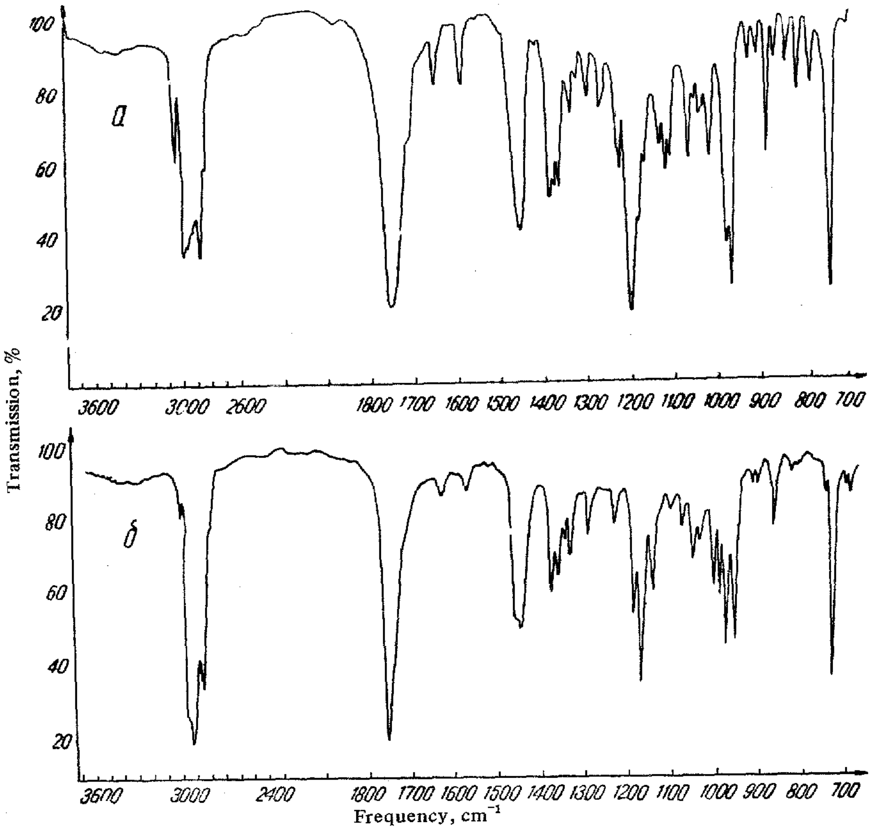
On chromatographing the resin on a column of alumina in addition to badkhysin [1–3] and badkhysinin [4], a crystalline substance with the composition $C_{15}H_{20}O_2$, mp 140–141° C (from aqueous ethanol) was isolated which we have called feropodin. As the IR spectrum (figure, a) shows, the substance exhibits absorption bands at (cm^{-1}) 1750 and 1195 (γ-lactone ring) and also at 1645, 1587, 975, 960, and 735 (double bonds). There are no OH or ketonic CO groups. The IR spectrum of the substance has a maximum at λ 264 mμ (log ε 3.82). On the basis of this maximum, we came to the conclusion that feropodin contains a conjugated system of double bonds.

The presence of a lactone ring in feropodin was confirmed by its solubility in alkali on heating. When the alkaline solution was acidified, α-isoferopodin, $C_{15}H_{20}O_2$, mp 115–117° C (from aqueous ethanol) was obtained. The IR spectrum of the latter (figure, b) had bands at (cm^{-1}) 1760 and 1177 (CO group of a γ-lactone) and 1640, 1580, 995, 980, 962, and 732 (double bonds). The UV spectrum of α-isoferopodin had the maximum of a conjugated system (λ 262 mμ, log ε 3.7).

The NMR spectrum of feropodin has a singlet at τ 9.1 (3 H) which is characteristic for an angular methyl group $(CH_3-\overset{|}{\underset{|}{C}}-)$. This means that the substance has a bicyclic carbon skeleton.

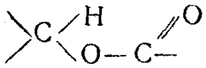
The absence from the UV spectrum of a maximum in the 210–224 mμ region and the appearance in the NMR spectrum of a doublet with a center at τ 8.78 (J = 7 Hz; 3 H) shows the presence in the substance of a secondary methyl group (CH_3-CH) at C_{11}. A singlet signal with τ 8.02 and an intensity of three proton units corresponds to a vinylmethyl group. Hence, one double bond in the molecule of feropodin is adjacent to a methyl group $(CH_3-\overset{|}{C}=)$. Thus, the double bond may be either at C_4-C_5 or at C_4-C_9. In the first case the double bond is trisubstituted and in the second case tetrasubstituted.

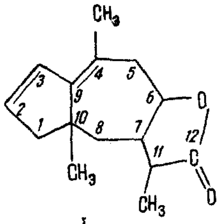


IR spectra of feropodin (a) and of α-isoferopodin (b) (paraffin oil)

The IR spectrum of feropodin exhibits no strong bands characteristic of a trisubstituted double bond (in the 790–840 cm^{-1} region) and therefore the presence in the system under investigation of a tetrasubstituted double bond at C_4–C_9 is more probable. A band at 735 and a doublet with maxima at 960–975 cm^{-1} show that the second double bond has a secondary-secondary nature.

In the NMR spectrum there are two multiplets of vinyl protons in the weak field with centers at τ 4.55 and 4.23, their area being equal to two proton units. The shift between the signals of the vinyl protons is due to conjugation.

It is known that in sesquiterpene lactones the isopropyl group present at C_7participates in the form of the lactone ring. Consequently, the lactone ring may be present at C_6–C_7or at C_7–C_8. The quartet observed in the NMR spectrum with a center at 5.2 τ  ; J_1 = 5 Hz; J_2 = 9 Hz: 1 H) excludes the possibility of the presence of a lactone ring at C_7–C_8. The nature of the splitting indicates interaction, at least, with two neighboring protons and permits the lactone ring to be assigned to the C_6–C_7 position



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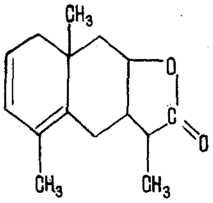

II

On the basis of the results presented, the alternative hypothetical structures I and II may be put forward for feropodin.

Structure I is more probable from the point of view of biogenesis.

Experimental

Isolation of feropodin. One hundred fifty grams of the resin was dissolved in benzene and transferred to a column of alumina (2000 g, activity grade III–IV) 100 cm high. Elution was carried out with petroleum ether (1700 ml) and mixtures of petroleum ether and diethyl ether (9:1; 8:2; 7:3; 6:4; 1:1, and so on). The volume of each fraction was 100 ml. From the fractions obtained on elution with petroleum ether–diethyl ether (6:4) was isolated a crystalline substance with mp 140–141° C (from aqueous ethanol). Chromatography in a thin layer of Al_2O_3 (inert solvent–chloroform) gave one spot with R_f 0.67. Yield 0.05 g (~0.033% of the weight of the resin).

Found, %: C 77.63; H 8.88. Calculated for $C_{15}H_{20}O_2$, %: C 77.59; H 8.62.

Saponification of feropodin. A solution of 0.02 g of feropodin in 5 ml of ethanol was treated with 5 ml of 5% aqueous KOH solution and the mixture was boiled on the water bath for 30 min. The ethanol and part of the water were evaporated off and the residue was cooled and acidified with HCl. On standing at room temperature the acidified solution deposited crystal of α-isoferopodin with mp 115–117° C (from aqueous ethanol).

The IR spectra were recorded on a UR-10 spectrophotometer, the UV spectra on an SF-4a instrument, and the NMR spectra on a JNM 4H-100/100 MHz spectrometer in $CDCl_3$ solution with $(CH_3)_4Si$ as standard.

Conclusions

From the resin of the roots of Ferula oopoda (Boiss. et Buhse) Boiss. a new sesquiterpene lactone, feropodin, with the composition $C_{15}H_{20}O_2$, mp 140–141° C, has been isolated. The alternative hypothetical structures I and II have been proposed for feropodin.

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