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OOPODIN—A SESQUITERPENE LACTONE FROM THE ROOTS OF FERULA OOPODA

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In a further chemical investigation of the resin from the roots of Ferula oopoda (Boiss et Buhse) Boiss by chromatography on a column of alumina we have isolated a crystalline sesquiterpene lactone with the composition $C_{20}H_{26}O_4$, mp 127–128° C (from aqueous ethanol), which we have called oopodin.

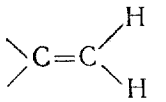
The UV spectrum of oopodin has a maximum at λ 233 mμ (log ε 4.35), which is characteristic for a system of conjugated double bonds. The IR spectrum of the substance (Fig. 1) shows bands at (cm^{-1}): 1760 (CO group of a γ-lactone), 1710 (CO group of an α,β-unsaturated ester), and 3035, 1643, 1600, 913, 895, 850, 840, 805, 760 (double bonds).

The nature of the ester group was elucidated by the saponification of oopodin with alkalis in ethanol. This yielded 2 sublimable acid with mp 44–45° C which gave no depression of the melting point in admixture with angelic acid, and a hydroxylactone with the composition $C_{15}H_{20}O_3$, mp 125–127° C (from aqueous ethanol). The IR spectrum of the saponified product had bands at (cm^{-1}): 3550 (OH group), 1760 (CO group of a γ-lactone), and 3035, 1640, 1600, 905, 813, 795 (double bonds). A mixture of the saponification product and the starting material melted at 106–113° C.

On the basis of what has been said above, it may be assumed that oopodin has three double bonds. One of them, secondary-tertiary, is present in the angeloyl group and the other two are conjugated with one another (λ_{max} 233 mμ).

The NMR spectrum of the substance under investigation (Fig. 2) has a singlet at τ 9.05, which is characteristic for an angular methyl group $\left(CH_3-\overset{|}{\underset{|}{C}}-;\ 3H\right)$ A doublet with a center at τ 8.73 (J = 6 Hz; 3H) is due to a secondary methyl group in a lactone ring ($CH_3-CH<$; at $C_{(11)}$). The doublet present in the IR spectrum with a center at τ 8.0 (J = = 3 Hz; 3H; $CH_3-CH=$) and a singlet at τ 8.07 (3H; $CH_3-C=$) are due to the vinyl methyls of the angeloyl group, the singlet signal being superposed on one component of the doublet.

In view of the presence of two signals of methyl groups in the NMR spectrum of oopodin (apart from the methyl signals from the angeloyl group), it may be concluded that the second double bond is present in an exocyclic methylene group (at $C_{(4)}$). The two singlets in the spectrum at τ 4.55 (1H) and 4.70 (1H) are due to the two vinyl protons of a


group.

The third double bond, conjugated with the primary-tertiary double bond, may be either secondary-secondary or secondary-tertiary. The IR spectra of oopodin and its saponification product have no strong bands permitting the presence of a secondary-secondary double bond to be inferred. The bands at 850, 845, 805, and 760 cm^{-1} in the spectrum of the saponification product characterize a secondary-tertiary double bond.

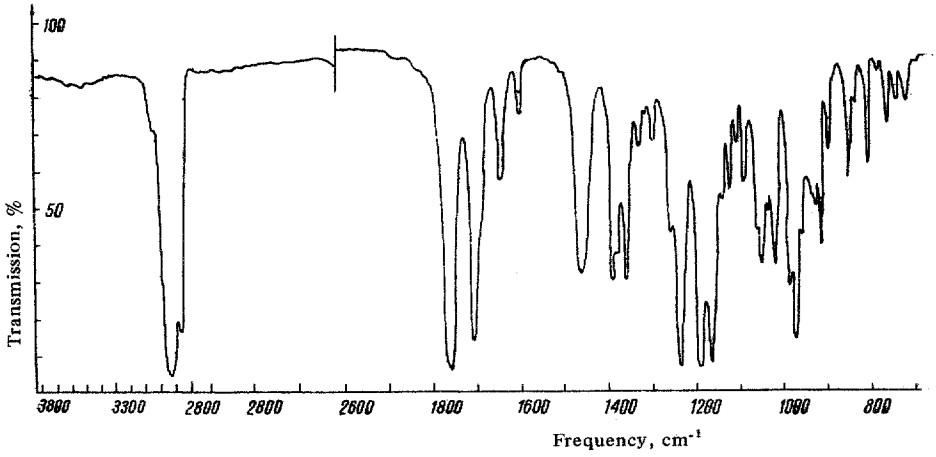


Fig. 1. IR spectrum of oopodin.

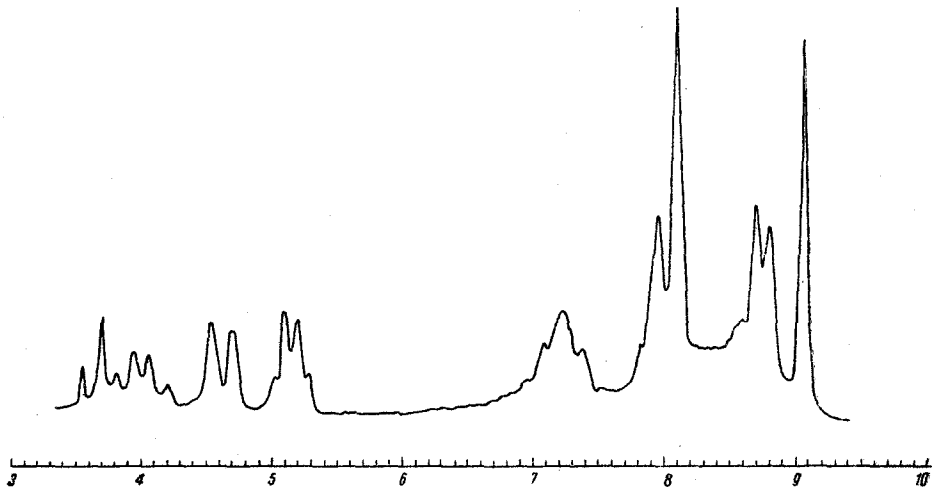
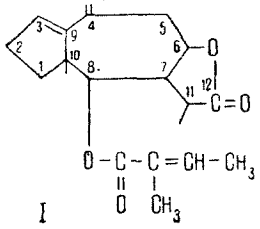


Fig. 2. NMR spectrum of oopodin.

The signals of the vinyl proton of the angeloyl group and of the vinyl proton at the secondary-tertiary double bond in the NMR spectrum are found in the τ 3.5–4.3 region. The signal with τ 5.15 and with an area of two proton units is apparently the result of the superposition of the signals of a proton at a lactone carbon atom and a proton at an ester group. This signal is completed by a doublet with a splitting constant of 6 Hz. Consequently it may be assumed that the signals overlapping one another probably have multiplet and doublet splitting. The NMR spectrum of saponified oopodin may serve as a confirmation of this. The signal due to the proton at the ester group in the spectrum of the latter is, as we expected, shifted in the strong-field direction and is found in the form of a doublet with a center at τ 6.44 (1H) with a splitting constant of 6 Hz. The nature of the splitting permits a position at $C_{(5)}$ or $C_{(8)}$ to be ascribed to it. In the first case the proton at the ester group occupies the allyl position with respect to the methylene double bond, and this must cause a considerable lowering (~0.55 τ) of the chemical shift [1,2]. However, no effect of this type is observed. Consequently, position $C_{(8)}$ is more likely for the ester group. The proton at the lactone oxygen atom in the NMR spectrum of saponified oopodin shows an unresolved multiplet signal with a center at τ 5.2. On the basis of this fact, we assign the $C_{(6)}$–$C_{(7)}$ position to the lactone ring.

The data presented permit the probable structure I to be proposed for oopodin



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Experimental

The IR spectra were recorded on a UR-10 instrument in paraffin oil, the UV spectra on an SF-4a spectrophotometer in 96% ethanol, and the NMR spectra on a JNM-C-60 MHz spectrometer (in solution in deuterated chloroform) with tetramethylsilane as standard. The microanalyses were performed by E. A. Sokolova in the Laboratory of the Chemistry of Plant Substances of the Botanical Institute of the Academy of Sciences of the USSR.

Isolation of oopodin. A solution of 100 g of the resin in 100 ml of benzene was chromatographed on a column of Al_2O_3 (1000 g, activity grade III–IV) 75 cm high. Elution was carried out with petroleum ether, mixtures of petroleum ether with diethyl ether (4:1, 3:2, 1:1, 1:2, 1:3, and 1:4), and ether. The volume of each fraction was 200 ml. The fractions obtained by elution with petroleum ether–diethyl ether (3:2) yielded oopodin with mp 127–128° C (from aqueous ethanol); IR spectrum, ν_{max}, cm^{-1}: 3035, 1760, 1710, 1643, 1600, 913, 895, 850, 840, 805, 760; UV spectrum: λ_{max} 333 mμ (log ε 4.35).

Found, %: C 72.57, 72.73; H 7.69, 7.92. Calculated for $C_{20}H_{26}O_4$, %: C 72.72; H 7.88.

Saponification of oopodin. A solution of 0.1 g of oopodin in 10 ml of methanol was treated with 5 ml of 5% aqueous KOH and boiled for 45 min. The methanol and part of the water were evaporated off and the residue was acidified with H_2SO_4, extracted with ether, and shaken with 0.5% aqueous sodium carbonate solution. The ethereal layer

was washed twice with water and was dried over Na_2SO_4. The residue after the distillation of the ether, a viscous oil, was dissolved in a mixture of petroleum ether and ether. On standing, crystals with mp 125-127° C (from aqueous ethanol) deposited.

IR spectrum, ν_{max}, cm^{-1}: 3550, 3035, 1760, 1640, 1600, 905, 813, 795.

Found, %: C 72.35; H 8.13. Calculated for $C_{15}H_{20}O_3$, %: C 72.55; H 8.12.

The sodium carbonate solution was acidified and extracted with ether. Treatment of the extracts by the method described above yielded a sublimable acid with mp 44-45° C giving no depression of the melting point with angelic acid.

Conclusions

From the resin of the roots of Ferula oopoda (Boiss. et Buhse) Boiss. a new sesquiterpene lactone $C_{20}H_{26}O_4$, mp 127-128° C, has been isolated which has been given the name oopodin. The probable structure I has been proposed for oopodin.

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