11,13-DEHYDRO-OOPODIN FROM THE ROOTS OF FERULA OOPODA

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Continuing chemical studies of Ferula oopoda (Boiss. et Buhse) Boiss. [1–8], by chromatographing the resin from the roots on a column of alumina we have isolated a sesquiterpene lactone with the composition $C_{20}H_{24}O_4$, mp 113–114° C (from aqueous ethanol). The IR spectrum of the substance (Fig. 1) has bands at 1765 cm^{-1} and 1670 cm^{-1} (α,β-unsaturated γ-lactone), 1705 and 1650 cm^{-1} (α,β-unsaturated ester), and 1650 and 1603 cm^{-1} (conjugated double bonds). The UV spectrum also shows the presence of these chromophores: λ_{max} 232 and 224 $m\mu$ (log ε 4.32, 4.33).

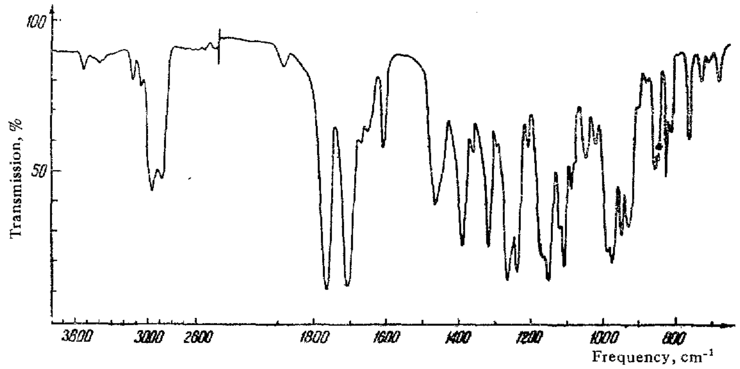

Fig. 1. IR spectrum of 11,13-dehydro-oopodin.

The presence of a lactone ring and of an ester group is confirmed by the saponification of the substance with alkali, which yielded an acid with mp 44–45° C, giving no depression of the melting point in admixture with angelic acid, and a hydroxylactone with the composition $C_{15}H_{18}O_3$, mp 152–153° C. The IR spectrum of the saponified product had bands at 3300 cm^{-1} (OH group), 1760 and 1660 cm^{-1} (α,β-unsaturated γ-lactone ring) and 1640 and 1605 cm^{-1} (conjugated double bonds.

The NMR spectrum* of the lactone with mp 113–114° C (Fig. 2) shows two doublets in the weak field with centers at τ 3.60 (J = 3 Hz, 1 H) and 4.40 (J = 3 Hz, 1 H), which are characteristic for an exocyclic methylene group in a lactone ring and permits the partial structure A to be ascribed to it.

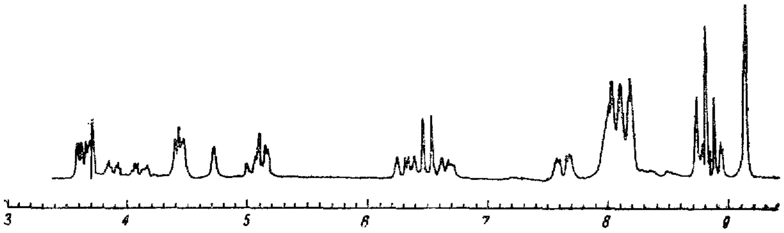

Fig. 2. NMR spectrum of 11,13-dehydro-oopodin.

The singlet at τ 9.13 (3 H) observed in the spectrum shows the presence of an angular methyl group $(CH_3-\overset{|}{\underset{|}{C}}-)$. The singlet at τ 8.18 (3 H, $CH_3-C=$) and the doublet with a center at τ 8.05 (3 H, J = 7 Hz; $CH_3-CH=$) belong to the vinyl methyls of the angeloyl group. The olefinic proton of the ester group appears in the form of a multiplet in the 3.98 τ region.

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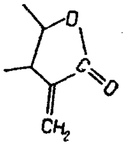
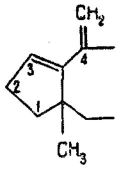
*The triplet with τ 8.80 (CH_3-), the quartet with a center at τ 6.48 ($-CH_2-$), and the singlet at τ 3.71 ($-OH$) are due to the protons of ethanol.



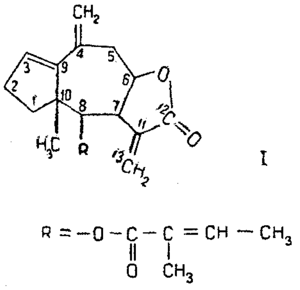
A

As the spectral features show, the substance apparently has four double bonds which confirm the results of hydrogenation. On exhaustive hydrogenation with Pd/C, the lactone adds 4 moles of hydrogen. One of the double bonds, present on the lactone ring, is methylenic, and a second double bond, located in the angeloyl group, is trisubstituted. The remaining two double bonds are conjugated with one another (λ_{max} 232 mμ, log ε 4.32); one of them is likewise methylenic. The signals with τ 4.45 (1 H) and 4.70 (1 H) show that the $> C{=}C\langle^{H}_{H}$ group is located at C_4. The fourth double bond must be either disubstituted or trisubstituted (more likely a trisubstituted double bond). The presence of bands at 798 and 823 cm^{-1} in the IR spectrum of the saponified product agrees well with the hypothesis put forward. In the NMR spectrum of the substance under investigation there is a triplet with a center at τ 3.67 $\left(J = 3\,\mathrm{Hz}, -C\langle^{H}_{C<}\right)$, due to an olefinic proton at C_3, the area of the signal being one proton unit. On the basis of these facts, we may propose the partial structure B for the substance under investigation



B

The signals from the protons adjacent to the lactone oxygen atom and in the ester group are superposed and are found at τ 5.08. In the NMR spectrum of the saponified product there is the singlet of a $CH_3{-}\overset{|}{\underset{|}{C}}{-}$ group at τ 9.24 (3 H), doublets of a $>C{=}C\langle^{H}_{H}$ group attached to the lactone ring with centers at τ 3.66 (1 H, J = 3 Hz) and 4.39 (1 H, J = 3 Hz), two singlets of a $>C{=}C\langle^{H}_{H}$ group at C_4, τ 4.58 (1 H) and 4.78 (1 H), and signals due to an olefinic proton at C_3 (in the 3.67–3.82 τ region). The signal of a proton in the ester group has undergone a diamagnetic shift in the spectrum of the saponified product. The doublet with a center at τ 6.47 (1 H, J = 6 Hz) permits this proton to occupy the C_8 position. The triplet with a center at τ 5.08 (1 H, J = 9 Hz) is due to the proton adjacent to the lactone oxygen atom at C_6.



I

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

Thus, the substance investigated is a new sesquiterpene lactone not previously described in the literature and has the structure of 11,13-dehydro-oopodin.

The reduction of 11,13-dehydro-oopodin with sodium borohydride in methanol solution leads to a mixture of substances from which the 11,13-dihydro derivative $C_{20}H_{26}O_4$ with mp 127–128° C (from aqueous ethanol) was isolated; its IR spectrum (ν 1760,1710,1643, and 1600 cm^{-1}) agreed completely with the spectrum of oopodin. A mixture of the two substances gave no depression of the melting point.

The IR spectra were recorded on an UR-10 instrument in paraffin oil, the UV spectra on an SF-4 spectrophotometer in 96% ethanol, the NMR spectra of 11,13-dehydro-oopodin on a JNM-4H-100-MC spectrometer (solution in deuterated chloroform containing ethanol), and the NMR spectra of the saponified product on a JNM-C-60M-C instrument ($CDCl_3$ solution with tetramethylsilane as standard).

The microanalyses were performed by E. A. Sokolova in the laboratory of the Chemistry of Plant Substances of the Komarov Botanical Institute, AS USSR.

EXPERIMENTAL

Isolation of 11,13-dehydro-oopodin. The chromatography of the resin on a column of alumina was carried out by the method described previously [8]. After the isolation of the oopodin, the subsequent fractions yielded a crystalline substance with mp 113–114° C (from aqueous ethanol).

Found, %: C 73.31; H 7.23. Calculated for $C_{20}H_{24}O_4$, %: C 73.17; H 7.32.

Saponification of 11,13-dehydro-oopodin. A solution of 0.1 g of the substance in 5 ml of ethanol was treated with 0.2 g of KOH in 5 ml of water. The mixture was heated in the water bath for 30 min, cooled, diluted with water, acidified with dil H_2SO_4, and worked up by a published method [4]. This gave angelic acid with mp 44–45° C and a hydroxylactone $C_{15}H_{18}O_3$ with mp 152–153° C (from a mixture of petroleum ether and ether).

Found, %: C 73.51, 73.53; H 7.33, 7.38. Calculated for $C_{15}H_{18}O_3$, %: C 73.17; H 7.31.

Hydrogenation of 11,13-dehydro-oopodin. A solution of 0.1 g of the substance in 10 ml of ethanol was exhaustively hydrogenated with 0.1 g of Pd/C. The hydrogenation consumed 28.5 ml of H_2, while the amount required for four double bonds is 27.2 ml. The ethanolic solution was filtered and distilled. The residue consisted of a noncrystallizing oil. This substance was not studied.

Reduction of 11,13-dehydro-oopodin with sodium borohydride. A solution of 0.1 g of the substance in 10 ml of ethanol was treated with 0.4 g of $NaBH_4$ in portions. Then it was left at room temperature for 30 min, acidified with dil H_2SO_4, and extracted with ether. The ethereal extract was washed with water three times, dried over Na_2SO_4, filtered, and distilled. The residue was a viscous oil which partially crystallized from a mixture of ether and petroleum ether on standing. The crystals were separated off and recrystallized from aqueous ethanol. Mp 127–128° C.

CONCLUSIONS

The roots of Ferula oopoda (Boiss. et Buhse) Boiss. have yielded a new sesquiterpene lactone having the structure of 11,13-dehydro-oopodin (I).

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