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A SESQUITERPENE LACTONE—SEMOPODIN—FROM THE SEEDS OF FERULA OOPODA

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Continuing our studies of the sesquiterpene lactones of Ferula oopoda (Boiss et Buhse) Boiss [1, 2], we have studied the seeds of this plant. From the seeds collected in July 1967 in the Nakhichevan ASSR (Azerbaidzhanian SSR) by extraction with chloroform we obtained a resin the chromatography of which on a column of alumina yielded a crystalline substance with mp 177-178° C which we have called semopodin.

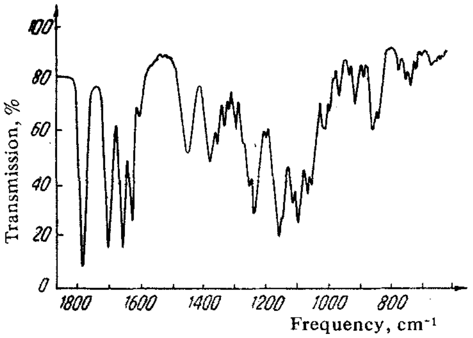


Fig. 1. IR spectrum of semopodin (paraffin oil).

According to the IR spectrum (Fig. 1), semopodin has absorption bands at 1785 cm^{-1} (γ-lactone ring), 1710 cm^{-1} (α, β-unsaturated ester group), 1660 cm^{-1} (conjugated keto group), and 1640 and 1610 cm^{-1} (double bond). The presence of a conjugated keto group is confirmed by the IR spectrum: λ_{max} 328 and 232 mμ (log ε 1.78 and 4.3). On the basis of the maximum in the UV spectrum it may be assumed that semopodin has an isoguaiane carbon skeleton. The features of the NMR spectrum confirm our assumption. In the NMR spectrum of the lactone (Fig. 2) in the region of methyl groups there is a singlet with τ 8.7 (3 H) which is characteristic for an angular methyl group $(CH_3 \; -\overset{|}{\underset{|}{C}}- \quad C_{10})$. This permits a bicyclic carbon sketeton to be ascribed to it.

The UV spectrum of sempoodin lacks a maximum in the 224-214 mμ region (a double bond conjugated with the CO group of a lactone generally appears in this region). Consequently in the NMR spectrum of the substance under investigation the doublet of a secondary methyl group (CH_3-CH) should appear. However, the spectrum has a singlet at τ 8.57 the area of which corresponds to three proton units. The value of the chemical shift (cs) of the singlet signal (8.57) is somewhat low. This displacement of the cs in the direction of the weak fields is apparently caused by the electronegativity of an oxygen atom (possibly by the presence of an oxide ring) [3-6].

The nature of the ester group was likewise established on the basis of the NMR spectrum. In the NMR spectrum there is a poorly resolved signal at τ 8.09 (J = 1.5 Hz); corresponding to a vinyl methyl group $(=\overset{|}{C}-CH_3)$ and a doublet of a secondary methyl group at a double bond $(=CH-CH_3)$ with a center at τ 7.98 (J = 7 Hz; 3 H). Each of the components of the doublet is poorly resolved (J = 1.5 Hz). The value of cs and the splitting of the signals are similar to those for the vinylmethyls of the angeloyl group in badkhyzin [7].

The vinyl proton of the angeloyl group is shown by a multiplet signal at τ 3.72. In the region of vinylmethyl groups there is yet another doublet with τ 7.85 (3 H; J = 2 Hz). This shows that one double bond conjugated with the keto group is adjacent to a methyl group at C_4. The second double bond is probably disubstituted.

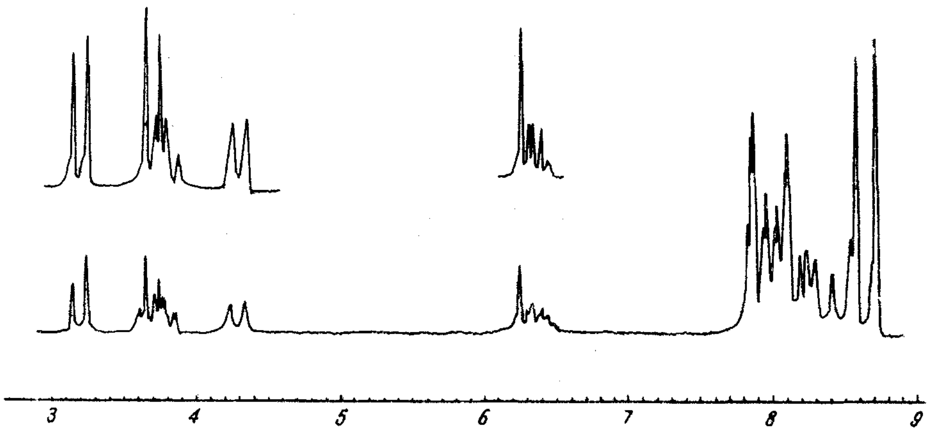
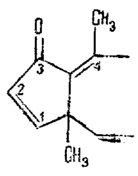


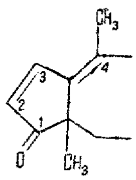
Fig. 2. NMR spectrum of semopodin.

In the weak field the NMR spectrum contains two doublets with centers at 3.19 τ (J = 10 Hz; 1 H at C_3) and 3.7 τ (J = 10 Hz; 1 H at C_2) belonging to the vinyl protons of a cyclopentene system. A doublet with a center at τ 3.7 is partially superposed on the multiplet signal of the vinyl proton of the angelicyl group.

The results of the interpretation of the NMR spectrum and of the maximum in the UV spectrum make it possible to propose one of the partial structures A and B for semopodin:



A



B

If the partial structure B is correct, the cs of the proton at C_3 should be shifted appreciably in the weak-field direction (~0.55 τ) [8, 9].

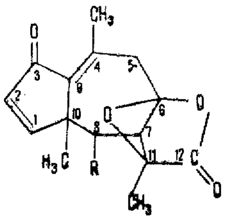
The hydrogenation of semopodin with Pt (from PtO_2) in ethanol led to a mixture of substances in the form of a viscous oil (~3 moles of hydrogen was added). Chromatography of this mixture on a column of Al_2O_3 (activity grade III–IV) yielded two fractions (I) and (II). Although these fractions were not individual substances, a study of their IR and UV spectra enabled us to establish that the keto group in the molecule of semopodin is present in the five-membered ring.

The IR spectrum of fraction I exhibited bands at 1782 cm^{-1} (CO of a lactone), 1730 cm^{-1} (CO of an ester), 1705 (CO-ketone group in a five-membered ring conjugated with one double bond), and 1610 cm^{-1} (double bond). The UV spectrum had the maxima of a conjugated ketone group at λ_{max} 328 and 232 mμ (log ε 2.46 and 3.266).

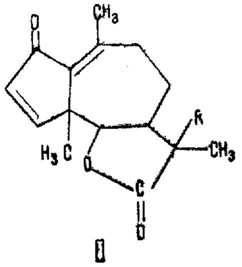
In the IR spectrum of fraction II absorption bands appeared at 1783 cm^{-1} (CO of a lactone), 1730 cm^{-1} (CO groups of a cyclopentanone and an ester grouping) and a shoulder at 1710 cm^{-1} (due to contamination with fraction I).

In the NMR spectrum there was a doublet with a center at τ 4.3 (1 H; J = 10 Hz), which is characteristic for a proton in an ester group. At the same time, this signal may also be caused (in spite of the low value of the chemical shift) by a proton adjacent to a lactone oxygen atom. No other signals were observed in the 4.5–6.0 τ region of the spectrum. In both cases the proton corresponds to C_8 position. This indicates the doublet splitting of the signal, which points to interaction with only one neighboring proton at C_7.

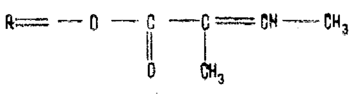
Summarizing all the results obtained, it may be concluded that probable alternative structures for semopodin are I and II.*



I



II



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

Experimental

Isolation of semopodin. Two hundred and thirty grams of the dry seeds were steeped in chloroform for 10 days and were then filtered off. The chloroform was distilled off in vacuum giving 1.6% (3.7 g) of resin. The residue was chromatographed on a column of Al_2O_3 (activity grade III–IV) 50 cm high and 3.5 cm in diameter. The substances were eluted from the column with petroleum ether, petroleum ether–ether (4:1; 3:2; 1:1; 1:2; 1:4), and ether,

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* The results of elementary analysis do not permit an unambiguous answer to the question of the molecular formula. On the basis of spectral results, the composition $C_{20}H_{22}O_6$ or $C_{20}H_{24}O_5$ is proposed.

25-ml fractions being collected. The fractions obtained by elution with the 1:1 mixture of petroleum ether and ether yielded 0.06 g of a crystalline substance with mp 177–178° C (from aqueous ethanol).

Hydrogenation of semopodin. A solution of 0.05 g of semopodin in 15 ml of ethanol was hydrogenated with Pt (0.05 g of PtO_2). The hydrogenation consumed 9 ml of hydrogen (10.3 ml of H_2 being required for three double bonds). The ethanolic solution was filtered and the ethanol was distilled off. The residue formed a noncrystallizing viscous oil, and this was chromatographed on a column of alumina (activity grade III–IV), 10 cm high and 1.9 cm in diameter. Elution was performed with 50 ml of petroleum ether, 100 ml of petroleum ether–ether (1:1), and ether. The fractions eluted with the petroleum ether–ether (1:1) were combined and the solvent was distilled off, giving fraction I. IR spectrum, ν_{max} cm^{-1}: 1782, 1730, 1710, 1610; UV spectrum, λ_{max}, mμ: 328 and 232 (log ε 2.46 and 3.266).

The ethereal eluates were combined and the ether was distilled off to give fraction II (ν_{max} 1783 and 1730, with a shoulder at 1710 cm^{-1}).

The IR spectra were recorded on a UR-10 instrument, the UV spectra of an SF-4A spectrophotometer, 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 seeds of Ferula oopoda (Boiss et Buhse) Boiss. a new sesquiterpene lactone with mp 177–178° C has been isolated which has been given the name semopodin. On the basis of the NMR, UV, and IR spectra semopodin has been ascribed the probable structure I or II.

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