THE STRUCTURE OF OOPODIN AND DEHYDRO-OOPODIN

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We have previously [1, 2] reported new sesquiterpene lactones from the roots of Ferula oopoda (Boiss. et Buhse) Boiss., which were called oopodin ($C_{20}H_{26}O_4$, mp 127-128°C) and dehydro-oopodin ($C_{20}H_{24}O_4$, mp 113-114°C). The results of a chemical investigation and of IR and UV spectroscopy, and also a partial interpretation of the NMR spectra permitted probable structures to be proposed for them based on the pseudoguaiane carbon skeleton.

However, in an analysis of the NMR spectra of saponified oopodin and dehydro-oopodin taken on a spectrometer with a resolving capacity of 100 MHz with integration of the areas of the signals, it was found that the proposed structures are not very accurate.

It must be mentioned that the NMR spectrum of oopodin recorded on an instrument with a working frequency of 60 MHz did not permit the area and the nature of the splitting of the individual protons to be determined because of the superposition of signals.

According to the structure proposed previously, the total area of the olefinic protons in the spectrum of the oopodin molecule is equivalent to 4 H: 1 H in a side chain, two belonging to an exocyclic methylene group, and the last H to a ring olefinic proton. Consequently, the area of the olefinic protons in the molecule of saponified oopodin should correspond to three protons.

However, the NMR spectrum of the saponified product (Fig. 1a) shows, in addition to the signals of the exocyclic methylene group, two other signals, the area of each of which corresponds to 1 H. Consequently, it may be assumed that the ring double bond is secondary–secondary, and not secondary–tertiary.

The signals at 5.16 ppm (1 H) and 5.40 ppm (1 H) observed in the NMR spectrum of saponified oopodin correspond to the protons of an exocyclic methylene group at C_1. The maximum at 233 nm (log ε 4.35) in the UV spectrum shows the presence in it of a conjugated system of double bonds. The doublet with a center at 6.22 ppm (1 H, $J_{2,3}=10$ Hz) and the quartet at 5.80 ppm (1 H, $J_{3,2}=10$ Hz, $J_{3,4}=6$ Hz) in the NMR spectrum of saponified oopodin are due to the protons of a double bond conjugated with a methylene double bond. In the region of methyl groups, the NMR spectrum has the singlet of an angular methyl group (0.74 ppm, $CH_3-\overset{|}{C}-$) and the doublet of a secondary methyl group (1.22 ppm, $J=6$ Hz, $CH_3-\overset{|}{C}H<$). The presence of a doublet and quartet (6.22 and 5.80 ppm) of vinyl protons together with the singlet of a $CH_3-\overset{|}{\underset{|}{C}}-$ group confirm that oopodin belongs to the group of sesquiterpene lactones of the eudesmane series. The spin–spin coupling constants of the quartet (10 and 6 Hz) permit the assumption that H-3 interacts with two neighboring protons. In addition, the NMR spectrum of oopodin [1] shows a signal with a center at 4.85 ppm and with an area of two proton units (result of the superposition of the H-4 and H-8 signals). This signal is completed by a doublet with a spin–spin coupling constant of 6 Hz. In the NMR spectrum of saponified oopodin, the signal of a proton at the OH group (H-4) is observed at 3.50 ppm ($J=6$ Hz). The nature of the splitting and the value of J for this proton show that it interacts with H-3 and makes it possible to assign position 4 to the ester group. A quartet with a center at 4.71 ppm ($J_{8,10}=10$ Hz, $J_{8,7}=7.5$ Hz) is due to the lactone proton (H-8) interacting with the two neighboring protons (H-10 and H-7). This position of the lactone ring is also confirmed by a

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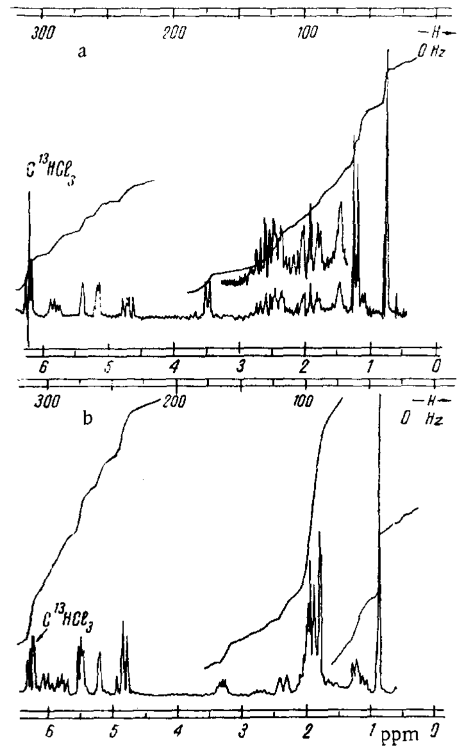


Fig. 1. NMR spectra of saponified oopodin (a) and dehydro-oopodin (b).

signal at 2.40 ppm (H-10). Because of its interaction with a neighboring proton (H-8), this signal is basically split into a doublet with a spin–spin coupling constant of 10 Hz. At the same time, each component of this doublet is additionally split into a triplet because of allyl interaction with the exocyclic methylene group at C_1.

As we have observed previously [1], the IR spectra of oopodin and of the saponified product show no bands characteristic for a secondary–secondary double bond. Bands at 850, 845, 805, and 760 cm^{-1} in the spectrum of oopodin and at 813 and 795 cm^{-1} in the spectrum of saponified oopodin are characteristic of a secondary–tertiary double bond. In this case, apparently, the phenomenon characteristic of the IR spectrum of tauremisin (vulgarin) [3] is observed.

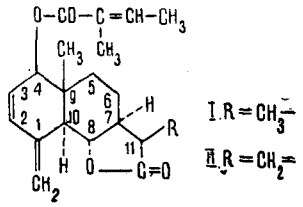
It is known that the reduction of dehydro-oopodin with sodium tetrahydroborate forms oopodin, in part [2]. In actual fact, the NMR spectrum of dehydro-oopodin (Fig. 1b) lacks the doublet of a secondary methyl group but shows two doublets with centers at 6.26 ppm (1 H, J = 3.5 Hz) and 5.49 ppm (1 H, J = 3.5 Hz) due to an exocyclic methylene group attached to a lactone ring (at C_{11}). In the region of olefinic protons, the spectrum has a doublet (at 6.28 ppm, 1 H, $J_{2,3}$ = 10 Hz) and a quartet (with a center at 5.78 ppm, 1 H, $J_{3,2}$ = 10, $J_{3,4}$ = 6 Hz) showing the presence of two ring olefinic protons in dehydro-oopodin (>C=C< with H on each carbon: H/C=C\H) and also the multiplet of a vinyl proton of an ester group (6.04 ppm, 1 H) and the signals of an exocyclic methylene group at C_1 (5.46 and 5.21 ppm, 1 H each).

The spectrum also shows the signals of an angular methyl group (CH_3—C—; 0.85 ppm) and of vinylmethyl groups corresponding to the ester group (triplet at 1.80 ppm, CH_3—C= and a doublet, each component of which is additionally split into a triplet at 1.90 ppm, J = 7 Hz, CH_3–CH=). A doublet in the spectrum (each component of which is also split into a triplet because of allyl coupling with the exocyclic methylene group at C_1) with a center at 2.35 ppm ($J_{10,8}$ = 10 Hz) is caused by H-10 interacting with the single neighboring proton on the lactone ring (at C_8). The multiplet at 3.28 ppm (1 H) in the spectrum of dehydro-oopodin relates to H-7.

It must be observed that in the NMR spectra both of oopodin [1] and of dehydro-oopodin the signals of the proton of the lactone ring and of that in the gem position to the ester group are partially superposed and appear at 4.85 ppm (2 H). In spite of this, it is possible to detect a doublet nature (4.80 ppm, J = 6 Hz) of the proton at the ester group, which is confirmed by the NMR spectrum of saponified dehydro-oopodin, in which the signal of the proton at the ester group shifts upfield, as we expected, while there is also a doublet at 3.51 ppm (J = 6 Hz). Now the lactone proton appears in the form of a quartet at 4.92 ppm ($J_{8,10}$ = 10 Hz, $J_{8,7}$ = 7.5 Hz). By comparing the nature of the splitting (quartet) and the spin–spin coupling constants ($J_{3,2}$ = 10 Hz, $J_{3,4}$ = 6 Hz) of H-3 with those for H-4 (doublet, $J_{4,3}$ = 6 Hz), it is possible to show that in the dehydro-oopodin molecule the ester group is located at C_4.

The results of a comparison of the spin–spin coupling constants of the protons at C_7, C_8, and C_{10} ($J_{8,7}$ = 7.5, $J_{8,10}$ = 10 Hz) of saponified oopodin and dehydro-oopodin show that they have the trans arrangement relative to one another.

Consequently, the stereochemistries of badkhysinin [4], of oopodin (I), and of dehydro-oopodin (II) are the same for the given carbon atoms, at least.



EXPERIMENTAL

The NMR spectra of saponified oopodin and of dehydro-oopodin were taken on a Varian HA-100D spectrometer in chloroform solution, and those of the saponified product of dehydro-oopodin on a JNM C-60 instrument in deuterated chloroform solution. Tetramethylsilane was used as internal standard, and the chemical shifts are given on the δ scale.

SUMMARY

The structures of oopodin and dehydro-oopodin have been corrected on the basis of spectral studies. These substances belong to the group of sesquiterpene lactones of the eudesmane series and have structures (I) and (II), respectively.

LITERATURE CITED

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