chemical shifts of the substances we used the chemical shift of the central peak of the ^{13}C triplet of the solvent, equal to 76.9 ppm relative to TMS taken as zero.

SUMMARY

The ^{13}C NMR spectra of artemin, dihydroartemin, and acetylartemin have been studied, and an assignment of the signals has been made on the basis of a comparative analysis of the chemical shifts of the ^{13}C nuclei.

LITERATURE CITED

1. S. V. Serkerov, Khim. Prir. Soedin., 452 (1982); 455 (1982).
2. N. D. Abdullaev, M. R. Yagudaev, V. A. Tarasov, Sh. Z. Kasymov, and G. P. Sidyakin, Khim. Prir. Soedin., 329 (1979).
3. G. Levy and G. Nelson, Carbon-13 in Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience, New York (1972).
4. F. W. Wehrli and J. Wirthlin, Interpretation of ^{13}C NMR Spectra, Heyden, London (1976).
5. P. S. Pregosin, E. W. Randall, and T. H. McMurry, J. Chem. Soc. Perkin Trans., No. 3, 299 (1972).

ARTAPSHIN — A NEW SESQUITERPENE LACTONE FROM *Artemisia fragrans*

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UDC 547.913

A new sesquiterpene lactone, $C_{15}H_{22}O_4$, which has been called artapshin (I) has been isolated from *Artemisia fragrans* Willd. The acetylation of (I) led to its diacetate $C_{19}H_{26}O_6$, mp 160-162°C (II). The saponification of (II) gave a dihydroxylactone $C_{15}H_{22}O_4$, mp 118-120°C. A structure has been proposed from artapshin on the basis of its chemical and spectral (IR and NMR) characteristics.

A substance with the composition $C_{15}H_{22}O_4$, which has not been possible to crystallize, has been isolated by chromatography on a column of alumina from the resin obtained by extracting the epigeal part of *Artemisia fragrans* Willd. (fragrant wormwood) gathered on the Apsheron peninsular in August, 1981.

The IR spectrum of the compounds has bands of OH groups (3420 cm^{-1}), of a γ-lactone ring (1760 cm^{-1}) and of a double bond (1670 cm^{-1}). The presence in the spectrum of strong bands at 910 and 970 cm^{-1} permits the conclusion that the molecule of the lactone contains an exomethylene group. Acetylation of the compound led to a diacetate with the composition $C_{19}H_{26}O_6$, mp 160-162°C (chloroform–hexane). The IR spectrum of the diacetate had maxima at (cm^{-1}), 1780 (C=O of a γ-lactone); 1740, 1250, 1240 (C=O of acetyl groups); and 1660, 970, 900 (exocyclic methylene groups). The saponification of the diacetyl derivative gave a dihydroxylactone, $C_{15}H_{22}O_4$, mp 118-120°C (chloroform–hexane). The IR spectrum of the latter showed the bands of OH groups (3200-3360 cm^{-1}), of the CO group of a γ-lactone ring (1780 cm^{-1}), and of a double bond (1660, 990, 967, 900, 890 cm^{-1}).

Judging from the NMR spectrum of the acetyl derivative (Fig. 1), the lactone under investigation was based on a eudesmane carbon skeleton. This is indicated by the following features revealed by the spectrum: a singlet (at 0.97 ppm, 3H, $CH_3-\overset{|}{\underset{|}{C}}-$) of an angular methyl group, and a triplet (at 4.12 ppm, $J_1 = J_2 = 11$ Hz, 1 H) of a lactone proton, the ratio of

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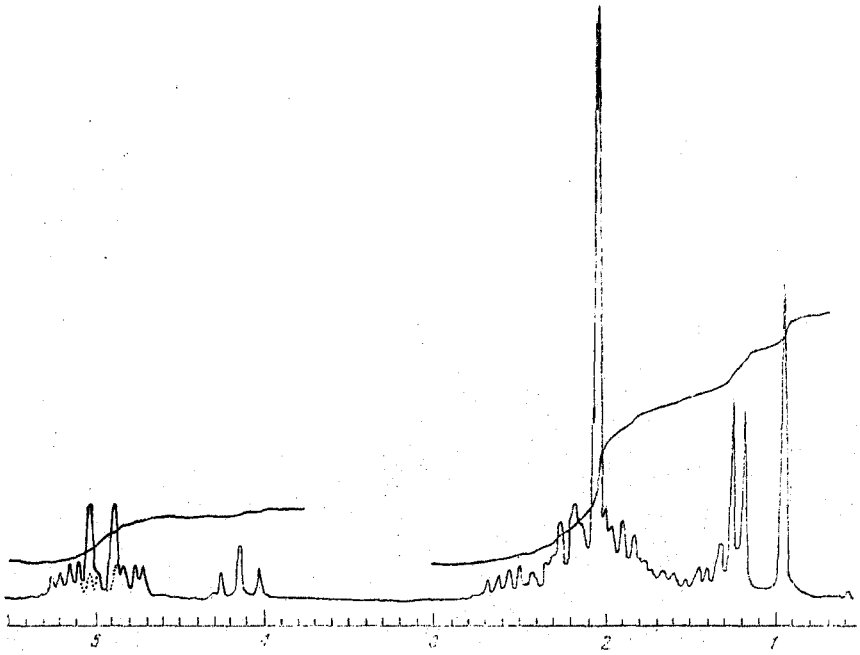


Fig. 1. NMR spectrum of artapshin diacetate.

the intensities of the components of which (1:2:1) show interaction with only two vicinal protons (H-5 and H-7). The splitting and the ratio of the intensities of the components of the signal of the lactone proton permit the lactone ring to be assigned to the C_6—C_7 position. The spin-spin coupling constant of H-6 gives grounds for stating that H-5, H-6, and H-7 have trans positions in relation to one another.

The presumed exomethylene group in the molecule of the lactone can be present at C-4 or C-11. Its presence at C-11 is, however, excluded, since the NMR spectrum lacks the doublet signals that are characteristic for an exomethylene group conjugated with the carbonyl of a lactone ring. The signals of the exomethylene group in the NMR spectrum of the diacetyl derivative appear in the form of two singlets with areas of 1 H each at 4.88 and 5.02 ppm. Thus, the methylenic double bond $CH_2=C<$ can be present only at C-4.

In addition to the $CH_3-\overset{|}{\underset{|}{C}}-$ singlet, in the region of methyl groups in the spectrum there is a doublet signal of a secondary methyl group at C-11 with its center at 1.25 ppm (J = 7 Hz, $CH_3-CH<$, 3 H). Singlets present in the spectrum of the diacetate at 2.05 and 2.06 ppm are due to the presence of the two acetyl groups.

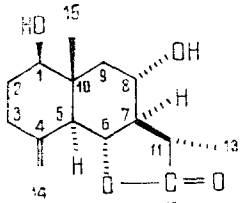
In the weak-field region of the spectrum two signals can be seen partially superposed on the singlets of the exomethylene group. They belong to two protons geminal to the acetyl groups. One of them appears in the form of a quartet at 4.80 ppm (J_1 = 5, J_2 = 11 Hz) showing interaction with two vicinal protons, and the other, in the form of a sextet at 5.10 ppm (J_1 = 5, J_2 = J_3 = 12 Hz), shows interaction with three protons.

The quartet signal permits one of the acetyl groups to be assigned to the C-1, C-3, or C-9 position. Its presence at C-3 is unlikely in view of the fact that, as is well known [1, 2], under these conditions the signal of this proton appears in a comparatively weak field ($\sim$0.40-0.50 ppm). A similar weak-field influence of a vicinal double bond has been detected in the NMR spectra of the diacetyl derivatives of erivanin [1] and isoerivanin (1,3-dihydroxyantenolide) [2], these being distinguished from one another only by the orientation of the OH group at C-1 [1]. Furthermore, when an acetyl group is present at C-3, the signals of the exomethylene group at C-4 also shift downfield [1, 2]. The presence of the acetyl group at C-9 is also excluded, since the sextet splitting and the ratio of the intensities of the components of the signals of the second geminal proton do not agree with any of the free positions (C-1, C-2, C-3, or C-8).

In order that the multiplicities and ratios of the intensities of the components of the signals of the protons geminal to the acetyl groups should correspond to the number of interacting vicinal protons, the hydroxy groups must be present at C-1 and C-8 in the molecule of the lactone under investigation.

The spin-spin coupling constants of H-1 (J_1 = 5, J_2 = 11 Hz) and H-8 (J_1 = 5, J_2 = J_3 = 12 Hz) indicate the β and α orientations of the hydroxy groups, respectively.

A comparison of the physicochemical and spectral properties of the lactone isolated and its derivatives with those of known sesquiterpene lactones have shown that the substance is new, and the name artapshin (I) is proposed for it.



I

A similar structure has been proposed for the deacetyldihydro-β-cycloisopyrethrosin, obtained on the alkaline hydrolysis of dihydro-β-cyclopyrethrosin [3]. The reference [3] does not give all the chemical shifts (including spin–spin coupling constants) of the signals in the NMR spectrum of deacetyldihydro-β-cycloisopyrethrosin and its diacetyl derivative, which makes it impossible to compare them with those for artapshin and its diacetate. We have therefore compared their properties. Thus, artapshin is a viscous oily substance, while deacetyldihydro-β-cycloisopyrethrosin has mp 196-197°C. Both compounds form diacetyl derivatives, but these have mp 160-162°C and 148-149°C, respectively. This shows that the substances are different. Artapshin and diacetyldihydro-β-cycloisopyrethrosin are apparently stereoisomers, differing only by the orientation of the methyl group attached to the lactone ring. This point of view is confirmed by the production on the saponification of diacetylartapshin of a crystalline dihydroxylactone with mp 118-120°C, likewise differing from deacetyldihydro-β-cycloisopyrethrosin (mp 196-197°C).

EXPERIMENTAL

IR spectra were taken in paraffin oil on a UR-20 spectrophotometer, NMR spectra on a HA-100D spectrometer in deuterated chloroform, O — TMS, δ scale.

Isolation of Artapshin. The air-dry ground epigeal part of *Artemisia fragrans*, gathered on the Apsheron peninsula (500 g) was extracted twice (for three days each time) with acetone. The acetone extract was filtered and evaporated. The residue consisted of 35.73 g of a dark green resin, which was chromatographed on a column (90 × 5 cm) of alumina with activity grade III. The volume of each fraction was 300 ml. Elution was performed with petroleum ether (40-70°C, 40 fractions) and with mixtures of petroleum ether and diethyl ether in ratios of 4:1 (16 fractions) and 3:2 (13 fractions) with diethyl ehter (10 fractions), withmixtures of petroleum ether and chloroform in ratios of 3:2 (10 fractions) and 1:4 (40 fractions), with chloroform (54 fractions), and with acetone (25 fractions). Fractions 12-40, eluted by petroleum ether–chloroform (1:4) were combined and rechromatographed on a column (2,5 × 3.5 cm) of alumina (activity grade II). The volume of each fraction was 250 ml. Elution was performed with chloroform. The chromatography of fractions 7 and 8 on a plate showed a single spot with R_f 0.87 (Al_2O_3, activity grade II, solvent chloroform–ethanol (99.5:0.5)).

Acetylation of Artapshin. A mixture of 0.1 g of artapshin, 2.5 ml of pyridine, and 3 ml of acetic anhydride was kept at room temperature for 24 h and was then diluted with 50 ml of water and evaporated in a porcelain dish on the water bath. The residue was dissolved in 10 ml of chloroform and the solution was filtered through a 15-cm layer of Al_2O_3 (activity grade II). Elution was performed with chloroform. The solvent was distilled off giving as residue a crystalline substance which was recrystallized from chloroform–hexane. mp 160-162°C.

Saponification of Artapshin Diacetate. A solution of 0.05 g of artapshin diacetate in 10 ml of 5% aqueous KOH was heated on the water bath for 2 h and was left at room temperature for 16 h. Part of the water was evaporated off and the remaining solution was acidified with dilute sulfuric acid and extracted with ethyl acetate. The extract was dried over Na_2SO_4, filtered, and evaporated. The residue was recrystallized from a mixture of chloroform and hexane. mp 118-120°C.

SUMMARY

A new sesquiterpene lactone with composition $C_{15}H_{22}O_4$, which has been called artapshin, has been isolated from *Artemisia fragrans* gathered on the Apsheron peninsula. A structure has been proposed for artapshin.

LITERATURE CITED

1. S. V. Serkerov, Khim. Prir. Soedin., 488 (1979).
2. S. P. Pathak, B. V. Bapat, and G. H. Kulkarni, Indian J. Chem., 8, 1147 (1970).
3. R. W. Doskotch, F. S. El-Feraly, and C. D. Hufford, Can. J. Chem., 49, 2103 (1971).

OXIDATIVE TRANSFORMATIONS OF CEMBRANE DITERPENOIDS.

VI. EPOXIDATION OF ISOCEMBROL

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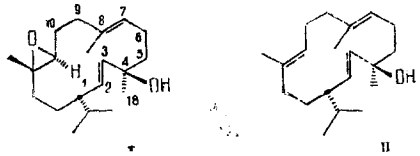
The stereochemistry of the epoxidation of the diterpene alcohol isocembrol has been studied. The main direction of attack of peracids is the C_{11} double bond of isocembrol, with the predominant formation of the 11S,12S-epoxide. The ratio of the monoepoxyisocembrols does not change appreciably with a variation in the temperature of the reaction or in the peracid used. 11S,12S-Epoxyisocembrol has been isolated as a natural product from the oleoresin of the Siberian stone pine.

In communication [1] we reported the formation of 11S,12S-epoxyisocembrol (I) as the main product of the epoxidation of isocembrol (II) by peracetic acid. The structure and stereochemistry of this compound were shown by its conversion into the known 11S,12S-epoxycembrene on dehydration with phosphorus oxychloride in pyridine. The spectral characteristics of compound (I) coincided with those for trocheliophorol — a component of soft corals of *Sarcophyton* sp. [2], which enabled the stereochemistry of the latter to be obtained, this being latter confirmed by Carmely [3].



I II

In the present paper we give the results of a more detailed investigation of the epoxidation of isocembrol. As compared with the epoxidation of cembrene [4], this reaction leads to a more complex mixture of monoepoxides. The ease of identification of the epoxide (I) is due to its greater accessibility, since it is readily separated by chromatography from the other products — monoepoxides which, in TLC on Silufol, give two overlapping spots with R_f 0.72 and 0.62 (the R_f value of the epoxide (I) was taken as 1.00). The substances corre-

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