ARTESIN – A NEW SESQUITERPENE LACTONE FROM Artemisia santolina

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UDC 547.913.5 + 547.473.2

Continuing a study of the sesquiterpene lactones of the epigeal part of Artemisia santolina Schrenk [1], we have isolated a new lactone, $C_{15}H_{22}O_3$, which we have called artesin (I).

The IR spectrum of artesin (Fig. 1) has absorption bands in the following regions, ν_{max}, cm^{-1}: 3490 (OH), 1750 (carbonyl of a γ-lactone), 1660 ($-C=C-$). The substance dissolves on heating in alkalis and is precipitated unchanged from an acid medium.

With acetic anhydride artesin forms a monoacetyl derivative (II), $C_{17}H_{24}O_4$, in the IR spectrum of which the absorption band of a hydroxy group is absent and maxima characteristic for an acetyl group (1728 and 1250 cm^{-1}) have appeared, with the maximum for a γ-lactone carbonyl at 1770 cm^{-1}.

The NMR spectrum of artesin (Fig. 2) has signals due to the protons of an angular methyl group – a singlet at 1.02 ppm (3H) (here and below, the δ scale), which shows the bicyclic nature of the lactone. A doublet with its center at 1.14 ppm (3H, J = 10Hz) relates to the protons of a methyl group located on a secondary carbon atom ($>CH-CH_3$). A singlet at 1.75 ppm (3H) relates to the protons of a methyl group on a double bond. The lactone proton, located at C_6-C_7, is shown in the form of a weakly resolved doublet at 4.45 ppm (1H, J = 9 Hz), which shows the trans attachment of the lactone ring. A geminal proton to a hydroxy group is shown in the form of a quartet at 3.47 ppm (J = 10 Hz). The large spin–spin coupling constant shows that the hydroxy group has the equatorial orientation. The magnitude of the chemical shift of the angular methyl group shows that the hydroxy group is located at C_1.

The double bond in artesin is located at C_4-C_5, since in its NMR spectrum the lactone proton gives a signal in the form of a doublet, and signals of olefinic protons are absent.

In the NMR spectrum of acetylartesin there are signals of an angular methyl group – a singlet at 1.09 ppm (3H, $-\overset{|}{\underset{|}{C}}-CH_3$), a singlet at 1.75 ppm (3H, $-C=C-CH_3$), and a doublet with its center at 1.12 ppm (3H, J = 10 Hz), relating to the protons of a methylene group on a secondary carbon atom ($>CH-CH_3$). The

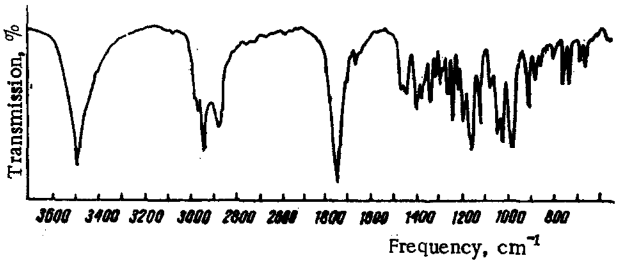

Fig. 1. IR spectrum of artesin.

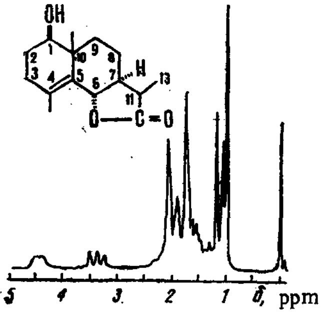

Fig. 2. NMR spectrum of artesin.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 733-735, November-December, 1972. Original article submitted April 16, 1972.

protons of the acetyl group appear in the form of a singlet at 1.96 ppm (3H). The signal of the lactone proton forms a doublet with its center at 4.7 ppm (1H, J = 8 Hz). An unresolved multiplet at 4.45 ppm (1H, W = 20 Hz) is due to the protons at C_1.

The oxidation of artesin with the Jones reagent [2] formed a substance (III) with the composition $C_{15}H_{20}O_3$. The IR spectrum of (III) showed an absorption band in the 1710-cm^{-1} region (ketonic carbonyl in a six-membered ring), and the band of a hydroxy group (3490 cm^{-1}) was absent.

The hydrogenation of (I) (Pd/C) gave a dihydro derivative with the composition $C_{15}H_{24}O_3$ in the IR spectrum of which the band at 1660 cm^{-1} was absent.

The spectra and melting point of artesin are similar to those of the dihydro derivative of taurin [3, 4] and the product of the oxidation of artesin (III) was identical, according to its IR spectrum and a mixed melting point, with taurin.

Consequently, artesin (I) is 1β-hydroxyeudesm-4(5)-en-6,12-olide.

EXPERIMENTAL

The IR spectra were taken on a Karl Zeiss spectrophotometer (tablets with KBr) and the NMR spectra on a C-60 HL instrument (in $CDCl_3$ with HMDS as internal standard).

Artesin (I). The epigeal part (unripe seeds, flowers, small stems) of Artemisia santolina Schrenk collected on August 23, 1970, in the south eastern Karakumy (Chardzhou Oblast, Turkmenian SSR) (23 kg) was extracted with chloroform (7 × 70 liters). The combined extracts were evaporated to dryness. The "resin" was dissolved in 60% ethanol, and the precipitate that deposited on standing was treated with petroleum ether. The residue (330 g) was chromatographed on a column of alumina (activity grade III-IV, 1 : 15). The column was eluted with benzene, benzene–ether (8 : 2; 7 : 3; 1 : 1), ether, and chloroform.

Fractions 1-10 were combined and rechromatographed on a column of alumina (activity grade III-IV, 1 : 20). Elution was performed successively with petroleum ether, petroleum ether–benzene (9 : 1; 8 : 2; 7 : 3; 1 : 1), benzene, and ether. The petroleum ether extracts (fractions 11-23), after evaporation, deposited crystals of artesin, $C_{15}H_{22}O_3$, mp 172°C (from ethanol), $[\alpha]_D^{27}$ + 49° (c 2; ethanol), M^+ 250 (mass spectrometry). Yield 1.4 g.

Acetylartesin (II). To a solution of 0.15 g of artesin in 2 ml of pyridine was added 2 ml of acetic anhydride. The mixture was left at room temperature for 15 h. Then the solvent was evaporated off, and the residue consisted of acetylartesin, $C_{17}H_{24}O_4$, mp 111-112°C (from ethanol).

Oxidation of Artesin (III). To a solution of 0.1 g of artesin in 5 ml of acetone at 0°C was added 0.8 ml of the Jones reagent. The mixture was kept in the cold for 15 min and at room temperature for 30 min. Then it was diluted with ice water, neutralized with sodium bicarbonate, and extracted with chloroform (7 × 50 ml). The chloroform extract was washed with water and the solvent was evaporated off. The residue consisted of taurin with mp 110°C.

Dihydroartesin (IV). The hydrogenation of an ethanolic solution of 0.1 g of artesin was performed in the presence of 50 mg of catalyst (Pd/C) for 2 h. Then the catalyst was filtered off and the solvent was evaporated off. The residue consisted of crystals with the composition $C_{15}H_{24}O_3$, mp 166-167°C (from ethanol).

SUMMARY

The epigeal part of Artemisia santolina Schrenk has yielded a new sesquiterpene lactone, artesin, $C_{14}H_{22}O_3$, having the structure 1β-hydroxyeudesm-4(5)-en-6,12-olide.

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