ARTELIN – A NEW SESQUITERPENE LACTONE FROM *Artemesia leucodes*

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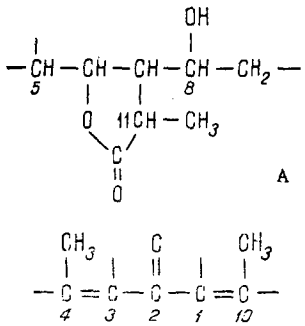
Continuing a study of the leaves and flower heads of Artemesia leucodes Schrenk. collected in the budding period [1], we have isolated a new sesquiterpene lactone – artelin (I), with the composition $C_{15}H_{18}O_5$ (M^+ 278), mp 228-229°C (ethanol), Rf 0.54 [Silufol, benzene–ethanol (8:2)].

The IR spectrum had absorption bands at, ν_{max}^{KBr}, cm^{-1}: 3420-3590 (OH), 1755 (C=O of a γ-lactone), 1680 (α,β-unsaturated cyclopentanone), and 1620 (double bond). The presence of a conjugated system was also shown by maxima in the UV spectrum at ($\lambda_{max}^{C_2H_5OH}$): 268 and 300 nm (log ε 3.42 and 3.31).

The mass spectrum of (I) was characterized by the peaks of ions with m/z (%): M^+ 278 (100), 263 (2), 245 (4), 204 (55), and others.

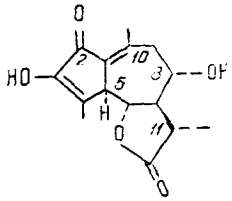
On treatment with acetic anhydride, (I) formed a diacetyl derivative with the composition $C_{19}H_{22}O_7$ (M^+ 362) in the IR spectrum of which the absorption band of OH groups was absent.

The mass spectrum of the diacetate had the peaks of ions with m/z (%): M^+ 362, 320 ($M - CH_2 = C = O$) (36), 278 ($M - CH_2 = C + O - CH_3COOH$) (88), 175 (100), and others.



A

B



I

The facts given above enable the oxygen functions of the molecule (I) to be determined: O–C=O of a γ-lactone ring, two OH groups, and a carbonyl group conjugated with a double bond.

The resonance lines in the PMR spectrum of artelin ($CDCl_3$, O – TMS, 300 MHz) were characterized by the following parameters (δ, ppm; J, Hz): 2.18 and 2.47 (s, 3 H each, CH_3-14 and CH_3-15, respectively); 1.46 (d, 3 H, ^3J = 7.2; CH_3-13); 3.28 (H-5, d, $^3J_{5,6}$ = 10.3); 3.56 (H-6, t, with Σ^3J = 20.3, where $^3J_{6,7}$ = 10.0 and $^3J_{6,5}$ = 10.3); 2.13 (H-7, q, with the line intensities in a ratio of 1:3:3:1, Σ^3J = 31.8, where $^3J_{7,6} = {}^3J_{7,8}$ = 10.0, and $^3J_{7,11}$ = 11.8); 3.59 (H-8, sextet, $^3J_{8,9\alpha}$ = 10.8; $^3J_{8,9\beta}$ = 2.3, and $^3J_{8,7}$ = 10.0); 2.39 (H-9β, q, ^2J = 14.0 and $^3J_{9\beta,8}$ = 2.3); 2.85 (H-9α, q, ^2J = 14.0 and $^3J_{9\alpha,8}$ = 10.0), and 2.54 (H-11, m). The complete interpretation of the PMR spectrum of (I), permitting these characteristics to be strictly assigned to concrete protons, was made on the basis of the results of the use of the method of multifrequency resonance.

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It was established from an analysis of the values of the chemical shifts of the protons and the spin-spin interaction between them that the artelin molecule included a fragment A, containing a secondary hydroxy group.

The presence in the spectrum of singlets at 2.18 and 2.47 ppm indicated that two methyl groups were located at double bonds and underwent an appreciable descreening influence of a conjugated carbonyl group, as is observed in the case of leucomisin [2, 3], austricin [4], and related compounds [6]. From this we find that the other member of the molecule (I) must be represented by fragment B. In the light of the doublet nature of the H-5 signal in the PMR spectrum, of the absorption band at 1680 cm^{-1} in the IR spectrum, and of the elementary composition, $C_{15}H_{18}O_5$, the linkage of fragments A and B can form only the basic guaiane skeleton (I).

With the presence of two double bonds in the artelin molecule, its PMR spectrum lacks the signal of an olefinic proton. In the mass spectrum of the diacetate of (I) there were two ions with m/z 320 formed as the result of the ejection of a ketene molecule ($M^+ - 42$, $CH_2=C=O$), which is characteristic for compounds containing acetoxy groups at double bonds. Furthermore, the treatment of artelin with $FeCl_3$ gave a positive reaction [2, 6]. These factors show that the second hydroxy group in the molecule of (I) is attached to C-3, with the formation of a double bond.

The trans linkage of the lactone ring at C-6 and C-7 and the α orientations of H-5, CH_3-13, and the hydroxy group at C-8 were established on the basis of an analysis of the values of the spin-spin coupling constants of the protons of fragment A of the (I) molecule.

Thus, artelin is the first sesquiterpene lactone of the austricin series containing a hydroxy group at the double-bonded C-3 atom, and it has the structure of 3,8α-dihydroxy-2-oxo-5α,7α(H),6β,11β(H)-guaia-1(10),3-dien-6,12-olide.

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