# NITROSIN — A NEW SESQUITERPENE LACTONE FROM *Artemisia nitrosa*

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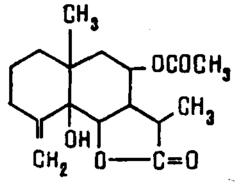
The flower heads, leaves, and small stems of *Artemisia nitrosa* Web. collected in August, 1980, in the valley of the R. Nura, Karaganda province, Kazakh SSR, have yielded three crystalline substances by treatment with hot water followed by extraction with chloroform and chromatography of the resin on a column of KSMG silica gel at a ratio of total material to support of 1:16 with elution by benzene—ether (4:1 and 1:1).

Substance (I) — $C_{17}H_{24}O_5$, mp 187-188°C (hexane—ether (1:1), $[\alpha]_D^{19}$ +37.7° (c 1.2; ethanol) proved to be a new sesquiterpene lactone and has been called nitrosin. IR spectrum, $\nu_{max}^{KBr}$, cm$^{-1}$: 3450 (—OH), 1775 (carbonyl of a γ-lactone), 1730 (carbonyl of an ester group), 1650 ($>C=C<$), 1460, 1380, 1220.

The PMR spectrum (Bruker WP-200 SY, 200.13 MHz, $CDCl_3$, 0 — TMS) characterized the presence in the structure of a tertiary methyl group — singlet at 0.93 ppm (3 H); a secondary methyl group — doublet at 1.19 ppm (3 H; J = 6 Hz); the methyl of an acetyl group — singlet at 1.99 ppm (3 H); the proton of a hydroxy group — singlet at 1.90 ppm (1 H); a lactone proton — doublet at 4.43 ppm (1 H, J = 12 Hz); the protons of an exocyclic methylene group — signals at 5.02 and 5.07 ppm (1 H each); and a hemiacyl proton — doublet of doublets at 5.39 ppm (1 H; $J_1$ = 6.5 Hz, $J_2$ = 2.5 Hz).

Substance (I) was not acetylated by acetic anhydride in pyridine and was not oxidized by chromium trioxide, which indicates the presence of a tertiary hydroxy group in its structure. On the basis of the physicochemical constants obtained, spectral characteristics, and the results of their comparison with literature information [1-5], we suggest for nitrosin the structure of 8-acetoxy-5-hydroxyeudesm-4(15)-en-6,12-olide (I) as the most probable.



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Substance (II) — $C_{15}H_{18}O_3$, mp 170-172°C (ethanol), $[\alpha]_D^{20}$ −173° (c 0.2; ethanol). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 240 nm (ε 5880). The IR spectrum contained absorption bands in the 1875 cm$^{-1}$ region (carbonyl of a γ-lactone and at 1665, 1635, and 1615 cm$^{-1}$ (double bonds conjugated with $>C=O$).

Substance (III) — $C_{15}H_{22}O_4$, mp 227-228°C (hexane—ether (1:1)). $[\alpha]_D^{20}$ +166° (c 1.2; ethanol), IR spectrum, $\nu_{max}^{KBr}$, cm$^{-1}$: 3465 (—OH), 3400-3340, 2950, 2880, 1780 (carbonyl of a γ-lactone), 1660 ($>C=C<$), 1456, 1380, 1370, 1315, 1275, 1260, 1235, 1185, 1155 cm$^{-1}$. When the lactone was acetylated with acetic anhydride in pyridine, a derivative with the composition $C_{17}H_{24}O_5$, mp 220-221°C (ethanol), was obtained which showed the absorption band of a hydroxy group in the IR spectrum. Consequently, the initial substance (III) contained hydroxy groups one of which was secondary and the other tertiary.

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From their physicochemical constants and IR, UV, and PMR spectra, substances (II) and (III) were identified as α-santorin and artemin, respectively [3, 4]. α-Santonin and artemin have not previously been isolated from Artemisia nitrosa.

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# NEW PSEUDOGUAIANOLIDE ARTESOVIN FROM Artemisia szowitsiana

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We have previously [1] reported on the isolation from the epigeal part of Artemisia szowitsiana (Bess.) Grossh. of α-santonin and artemisin. In the present paper we give information on the determination of the structure of a new pseudoguaianolide which has been called artesovin. It was isolated by chromatography on a column containing neutral alumina of the resin obtained by treating the aqueous fraction with chloroform after the isolation of the essential oil from fresh plant material of A. szowitsiana by the steam distillation method. Artesovin has the composition $C_{15}H_{20}O_3$*, mp 142-144°C (from aqueous ethanol). The molecular weight determined mass spectrometrically is 248.

The IR spectrum of artesovin contains absorption bands of the CO group of a γ-lactone (1780 $cm^{-1}$), the CO of a conjugated ketone group in a 5-membered ring (1713 $cm^{-1}$), and a double bond (1670 $cm^{-1}$). The UV spectrum confirmed the presence of a conjugated system: $\lambda_{max}$ 239 nm (log ε 3.86).

The NMR spectrum of artesovin showed the singlet of an angular methyl group at 1.20 ppm (3 H, $CH_3-\overset{|}{\underset{|}{C}}-$), doublets of secondary methyl groups at 1.12 ppm (3 H, J ≅ 8 Hz, $CH_3-CH<$) and 1.24 ppm (3 H, J ≅ 6 Hz, $CH_3-CH<$). One component of each doublet of the secondary methyl groups was superposed on the singlet of an angular methyl group. A lactone proton appeared in the form of a doublet at 3.80 ppm (1 H, J = 11 Hz), which shows its interaction with one vicinal proton (H-7).

On analyzing the IR, UV, and NMR spectra, it may be concluded that artesovin is based on a pseudoguaiane carbon skeleton. Consequently, it is represented by structure (I) or (II). However, one-proton doublets at 6.03 ppm (J = 6 Hz) and 7.65 ppm (J = 6 Hz) belonging to two olefinic protons (H-4 and H-3, respectively) of a double bond conjugated with a ketone group are similar to the signals of the olefinic protons of anhydrodehydroflexuosin A [2] and anhydrodehydrodihydropylchellin [3], which permits structure (I) to be assigned to artesovin.

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*The composition of artesovin was determined on the basis of its IR, UV, and PMR spectra.

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