11,13-DIHYDROARTEGLASIN A — A NEW GUAIANOLIDE FROM Artemisia argyi

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The isolation of the sesquiterpene lactones canin, chrysartemin B, isoridentin, matricarin, and hanphyllin from the flower heads and leaves of Artemisia argyi has been reported previously [1, 2].

Continuing the chemical study of this plant, by additional chromatography on alumina of the benzene fractions obtained in the isolation of matricarin and hanphyllin [2], with elution of the column by hexane–benzene (1:1), a colorless crystalline compound (I) has been isolated with the composition $C_{17}H_{22}O_5$, mp 165-166°C (hexane–acetone) M^+ 306. Its IR spectrum showed bands of the absorption of a γ-lactone carbonyl (1775 cm^{-1}) and of the carbonyl of an ester group (1738 and 1242 cm^{-1}). The mass spectrum contained, in addition to the peak of the molecular ion, peaks with m/z 264 (M–42) and 246 (M–60). These facts, and also the presence in the PMR spectrum of a three-proton singlet at 1.91 ppm and of a one-proton sextet of a gem-acyl proton with its center at 4.86 ppm, showed that the lactone molecule contained a characteristic group of signals relating to the basic lactone skeleton: a three-proton doublet at 1.26 ppm ($>CH{-}CH_3$, J = 6 Hz), two three-proton singlets at 1.55 ppm ($CH_3{-}C{-}O$), and 1.65 ppm ($CH_3{-}C{=}C$), a one-proton doublet at 2.65 ppm (J = 11 Hz, proton at C_5), a one-proton singlet at 3.23 ppm (gem-epoxide proton) and a one-proton triplet with its center at 3.57 ppm (^3J = 10 Hz, lactone proton).

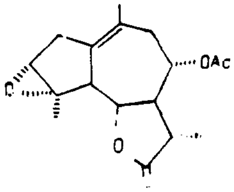
With the given composition, spectral characteristics, and functional groups, lactone (I) had to have a guaiane carbon skeleton. The absence from the PMR spectrum of (I) of the signal of an olefinic proton and the nature of the splitting of the lactone proton and the value of its spin–spin coupling constant showed the position of the double bond at $C_1{-}C_{10}$ and of the lactone ring at $C_6{-}C_7$ and also its trans-linkage.

The chemical shift of the signals of the protons of the methyl group (at 1.55 ppm) and that of the gem-epoxide proton determined the position of the epoxide group at $C_3{-}C_4$.

An analysis of the spectral characteristics of (I) showed that they were close to those of arteglasin A (II), with the only difference that the PMR spectrum of (II) contained the signals of the protons of an exomethylene group conjugated with the carbonyl of the lactone ring and lacked the signals of the protons of a methyl group at a secondary carbon atom, while in the mass spectrum of (II) the peaks of the molecular ion and of the corresponding fragmentary ions that were observed were displaced in the direction of lower masses by 2 m/z [3, 4].

On the basis of what has been said above, it was possible to conclude that lactone (I) was a dihydro derivative of arteglasin A (II) at the $C_{11}{-}C_{13}$ carbon bond. This conclusion received independent confirmation in the following way. Arteglasin A, which we had obtained earlier in establishing the structure of the guaianolide ajadin [5], was reduced with sodium tetrahydroborate by a published method [6] with the formation of a product analogous to the natural compound.

Consequently, lactone (I) had the structure 8α-acetoxy-3,4-epoxyguaian-1(10)-en-6,12-olide.



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DITERPENE ENDOPEROXIDES FROM THE NEEDLES OF Abies sibirica

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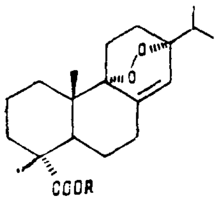
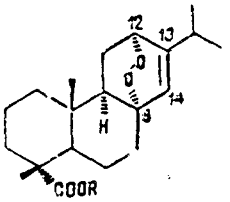
The main components of the acid fraction of an ethereal extract of the needles of the Siberian fir Abies sibirica Ledb. are triterpenoids and fatty and resin acids [1]. Continuing an investigation of the components of an extract of this fir, we have established that it contained 9α,13α-epidioxyabiet-8(14)-en-18-oic acid (I) and 8α,12α-epidioxyabiet-13-en-18-oic acid (II), known previously as products of the photooxidation of palustric [2] and levopimaric [3, 4] acids, respectively. They were isolated in the form of the methyl esters (III) and (IV) by the chromatography on silica gel of the methylated weak-acid fraction [1] with yields of 0.05 and 0.03% of the air-dry needles.



I. R-H

III. R = CH_3



II R=H

IV R=CH_3

Ester (III) had mp 123-125°C (from hexane), $[\alpha]_D^{22}$ −60° (c 0.3; $CHCl_3$); according to the literature [5]: mp 123-125°C, $[\alpha]_D^{22}$ −75°. It was identified by comparison with an authentic sample using TLC and PMR spectroscopy. Ester (IV) had mp 95-98°C (from methanol), $[\alpha]_D^{22}$ +90° (c 0.17; ethanol). According to the literature [3]: mp 96-98°C, $[\alpha]_D$ +93.5° (ethanol). Mass spectrum (m/z): 348 (M^+, 2%), 316 ($(M-O_2)^+$, 100% PMR spectrum (200.13 MHz, $CDCl_3$, ppm)): 0.54 (3H, s, CH_3-10), 1.05 and 1.09 (3H each, doublets with J = 7 Hz each, $-CH(C\underline{H}_3)_2$), 1.12 (3H, s, CH_3-4), 3.65 (3H, s, $COOCH_3$), 4.48 (1H, d.d.d, J = 4.3, 1.6, and 1.6 Hz, H-12), 5.83 ppm (narrow multiplet, H-14). On double resonance with suppression of the signal at 5.83 ppm, the multiplet at 4.58 ppm was converted into a doublet of doublets with J = 4.3 and 1.6 Hz. ^{13}C NMR spectrum (ppm): 74.56 (d, C-12), 76.90 (s, C-8), 124.59 (d, C-14), 140.00 (s, C-13).

Acids (I) and (II) and their methyl esters were not previously known as natural compounds. The origin of these acids is apparently connected with the photooxidation of palustric and levopimaric acids, respectively, in the growing needles with chlorophyll as sensitizer [6]. This process has been modeled by Moore [3] in vitro on levopimaric acid.

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