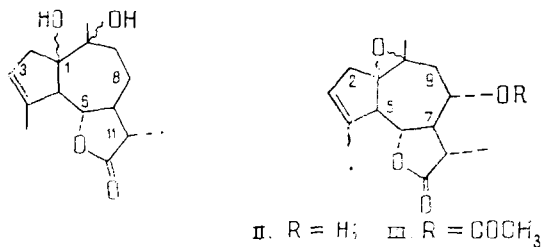


The PMR spectrum of (II) (C_5D_5N , 0 - TMS) was characterized by the following signals (ppm): 1.27 (3 H, s, CH_3-C-C); 1.66 (3 H, d, $^3J = 6.8$ Hz, CH_3-CH); 2.02 (3 H, br.s, $CH_3-C=C$); 4.1 (1 H, m, $CH-OH$); 4.20 (1 H, t, $\Sigma^3J = 21$ Hz, H-6); 5.45 (1 H, br.s., $H-C=C-CH_3$); and 6.30 ppm (1 H, d, $^3J = 6$ Hz, $CH-OH$).

The acetylation of (II) with acetic anhydride in pyridine gave a monoacetyl derivative (III) with mp 146-148°C. In the PMR spectrum of (III) ($CDCl_3$, 0 - TMS) characteristic signals were located at (ppm): 1.27 (3 H, d, $^3J = 6.7$ Hz, CH_3-CH); 1.36 (3 H, s, CH_3-C-C); 1.92 (3 H, br.s, $CH_3-C=C$); 2.08 (3 H, s, OAc); 4.11 (1 H, t, $\Sigma^3J = 20$ Hz, H-6); 5.20 (1 H, sx, $^3J = 10$, 10, and 4 Hz, $CH-OAc$, H-8); and 5.53 (1 H, br.s, $H-C=C-CH_3$, H-3). These characteristics of compound (III) correspond to those of globicin [5, 6].

On the basis of these facts was established that the second new guaianolide (II) corresponded to the structure of deacetylglabacin.



LITERATURE CITED

1. S. S. Danyluk and W. G. Schneider, *Can. J. Chem.*, **40**, 1777 (1962).
2. M. A. Irwin and T. A. Geissman, *Phytochemistry*, **8**, 305 (1969).
3. F. Bohlmann, A. Suwita, H. Robinson, and R. M. King, *Phytochemistry*, **20**, 1887 (1981).
4. S. M. Adekenov, G. M. Kadirberlina, A. D. Kagarlitskii, M. N. Mukhametzhano, A. A. Fomichev, and N. I. Golovtsov, *Khim. Prir. Soedin.*, 795 (1984). [Following paper].
5. R. B. Bates, V. Prochazka, and Z. Cekan, *Tetrahedron Lett.*, 877 (1963).
6. V. Prochazka, Z. Cekan, and R. B. Bates, *Collect. Czech. Chem. Commun.*, 1203 (1963).

ARLATIN — A NEW SESQUITERPENE LACTONE FROM *Artemisia latifolia*

S. M. Adekenov, G. M. Kadirberlina,
A. D. Kagarlitskii, M. N. Mukhametzhano,*
A. A. Fomichev, and N. I. Golovtsov

UDC 547.314:581.192

We have previously [1] found that the sum of the substances from *Artemisia latifolia* Lbd. inhibits the germination of the seeds of some plants to the extent of 78%. In order to establish the inhibiting principle we have investigated the individual components from this species of wormwood.

By extraction with acetone and chromatography of the combined substances on a column of type KSK silica gel (1:20) with elution by benzene-ether (4:1 and 1:1) and by ether we have isolated three crystalline substances from the flower heads and leaves of *A. latifolia* collected in the mass flowering phase in the gorges of the Abraly mountains, Semipalatinsk province, Kazakh SSR.

Substance (I) — $C_9H_6O_3$, mp 224-225°C (ethanol). Its IR spectrum has adsorption bands at (cm^{-1}) 3500 (OH groups), 3005, 2965, 2935, 1725 (C=O), 1620, 1590, 1515, 1465, 1420, 1325, 1165, 1130, 1075, 1010, 970, 920, 850. On the basis of its physicochemical constants and

*Deceased

Institute of Organic Synthesis and Coal Chemistry, Central Kazakhstan Branch, Academy of Sciences of the Kazakh SSR, Karaganda. Translated from *Khimiya Prirodnkh Soedinenii*, No. 6, pp. 795-797, November-December, 1984. Original article submitted July 4, 1983.

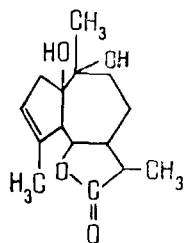
spectral characteristics, substance (I) was identified as umbelliferone [2, 3]. Umbelliferone is known as a factor of allelopathic action [4].

Substance (II) — $C_{15}H_{22}O_4$, mp 198–200°C (ethanol) — proved to be a new sesquiterpene lactone, which we have called arlatin. IR spectrum, ν_{\max}^{KBr} , cm^{-1} : 3480 (—OH); 1760 (carbonyl of a γ -lactone); 1435, 1380. The PMR spectrum (Tesla BS-497, $CDCl_3$, 0 — TMS) characterized the presence in the structure of: a secondary methyl group — doublet at 1.11 ppm (3 H, $J = 6$ Hz); a methyl group geminal to an oxygen atom — singlet at 1.21 ppm (3 H); a methyl group at a double bond — broadened singlet at 1.81 ppm (3 H); a lactone proton — triplet at 4.23 ppm (1 H, $J_1 = J_2 = 10$ Hz); the protons of hydroxy groups — singlet at 4.85 ppm (2 H); and an olefinic proton — singlet at 5.37 ppm (1 H).

The hydroxy groups were not acetylated by acetic anhydride in pyridine and were not oxidized by chromium trioxide, i.e., they were tertiary.

The ^{13}C NMR spectrum (Bruker WP-80, $CDCl_3$, 0 — TMS) contained three quartet, three triplet, four doublet, and five singlet signals which were assigned to 12 sp^3 -hybridized and 3 sp^2 -hybridized carbon atoms. The reaction of arborescin with oxalic acid gave a dihydroxy derivative identical in its physicochemical constants, spectral characteristics, and a mixed melting point with arlatin.

As a result of the investigations performed and a comparison of the results obtained with literature information [5, 6] we proposed structure (II) as the most probable for arlatin.



II

Substance (III) — $C_{16}H_{18}O_5$, mp 122–124°C (ethyl acetate), $[\alpha]_D^{19} +18.5^\circ$ (chloroform). UV spectrum: $\lambda_{\max}^{C_2H_5OH}$ 266, 325 nm. The IR spectrum contained absorption bands at (cm^{-1}) 3375 (OH group), 3180–3130, 2945, 2880, 1670 (C=O), 1585, 1500, 1440, 1395, 1360, 1335, 1255, 1215, 1195, 1150, 1115, 1090, 1055, 1045, 1000, 975, 920, 870, 840. In the PMR spectrum (Bruker WP-200 MHz, CD_3OD , 0 — TMS) there were doublets at (ppm) 1.18 (3 H, $J = 6$ Hz) — secondary methyl; multiplets at 1.72 ppm (1 H), and 2.04 ppm (2 H); a doublet of doublets at 3.64 ppm (1 H, $J_1 = 10$ Hz, $J_2 = 6$ Hz) and 3.72 ppm (1 H, $J_1 = 10$ Hz, $J_2 = 5.5$ Hz); a singlet at 4.05 ppm (H) — methoxy group; a triplet at 4.17 ppm (2 H, $J_1 = J_2 = 6$ Hz); and the signals of aromatic protons; doublets at 6.23 and 8.20 ppm (1 H each, $J = 9.6$ Hz), and a singlet at 6.54 ppm (1 H).

When (III) was acetylated with acetic anhydride in pyridine, a diacetate was obtained with the composition $C_{20}H_{22}O_7$, mp 80–85°C (benzene). UV spectrum: $\lambda_{\max}^{C_2H_5OH}$ 251, 259, 320 nm. IR spectrum: ν_{\max}^{KBr} 1750, 1708, 1600, 1245 cm^{-1} . The PMR spectrum showed the presence of a secondary methyl group — doublet at 1.02 ppm (3 H, $J = 6.5$ Hz); of a methoxy group — singlet at 3.89 ppm (3 H); of aromatic protons — doublets at 6.23 and 7.82 ppm (1 H each, $J = 9.6$ Hz); and a singlet at 6.89 ppm (1 H). In addition, there were singlets at 2.01 and 2.35 ppm (3 H each) — the methyls of acetyl groups — and a triplet at 4.35 ppm (2 H, $H_1 = 6.5$ Hz). A doublet of doublets appeared in the weak field at 4.10 ppm (2 H, $J_1 = 6$ Hz, $J_2 = 3$ Hz).

The study of the structure of substance (III) is proceeding.

LITERATURE CITED

1. S. M. Adekenov, A. N. Kupriyanov, M. N. Mukhametzhano, and K. A. Aituganov, "The growth-regulation activity of the extractive substances of some plants of the family Compositae," paper deposited at VINITI, No. 358-80 (1980).
2. R. D. H. Murray, Fortschr. Chem. Org. Nat., 35, 199 (1978).
3. R. V. Usynina, T. P. Berezovskaya, V. V. Dudko, and N. V. Erofeeva, in: The Investigation of Medicinal Preparations of Natural and Synthetic Origin [in Russian], Tomsk (1975), p. 3.

4. E. L. Rice, *Alleopathy*, Academic Press, New York (1974).
5. K. S. Rybalko, *Natural Sesquiterpene Lactones* [in Russian], Moscow (1978), p. 141.
6. R. G. Kelsey and P. Shafizadeh, *Phytochemistry*, **18**, No. 10, 1591 (1979).

SESQUITERPENE LACTONES OF *Inula caspica*

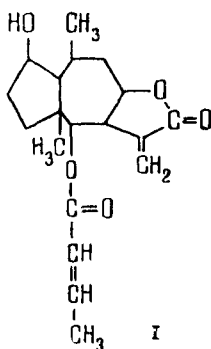
S. M. Adekenov, M. A. Abdykalykov,
A. D. Kagarlitskii, M. N. Mukhametzhanov,*
A. N. Kupriyanov, and K. M. Turdybekov

UDC 547.314:581.192:633.511

The flower heads and leaves of *Inula caspica* Blume. (Caspian inula) collected in the mass flowering phase in the Abrial mountains, Semipalatinsk province, Kazakh SSR, were exhaustively extracted with chloroform. The resin isolated was treated with 60% ethanol. The resulting precipitate was separated off, and the lactones were extracted from the aqueous ethanolic solution with chloroform. The combined extractive substances obtained inhibited the growth of mustard seeds by 62% and completely suppressed the germination of wheatgrass seeds. The combined substances were chromatographed on a column of type KSK silica gel at a ratio of material to support of 1:15. When the column was eluted with benzene and with benzene-ether (1:1), two crystalline substances were isolated.

Substance (I) — $C_{19}H_{26}O_5$, mp 220–222°C (ethanol), $[\alpha]_D^{18} +116.9^\circ$ (chloroform) was a new sesquiterpene lactone and we have called it incaspin. IR spectrum, ν_{max}^{KBr} , cm^{-1} : 3500 (—OH); 1750 (carbonyl of a γ -lactone); 1720, 1250 (ester group); 1670 (>C=C<). When (I) was dehydrogenated over 30% Pd-C at 330°C, chamazulene was obtained.

The PMR spectrum (taken on a Tesla BS-497 instrument in $CDCl_3$, 100 MHz, 0 — TMS) showed the following signals: singlet at 0.90 ppm (3 H) — angular methyl; doublet at 1.87 ppm (3 H) — secondary methyl group; doublet at 2.14 ppm (3 H) — methyl at a double bond of an ester group. A multiplet at 3.95 ppm (1 H) was assigned to H_6 ; a triplet of doublets at 4.57 ppm (1 H, $J_1 = 2$ Hz, $J_2 = 5$ Hz) to a lactone proton; a singlet at 4.70 ppm (1 H) to a hydroxylic proton; and doublets at 5.53 and 6.05 ppm (1 H each, $J_1 = J_2 = 2$ Hz) to the protons of an exocyclic vinyl group conjugated with the carbonyl of a γ -lactone. A singlet at 5.32 ppm (1 H) and a quartet at 5.58 ppm (1 H, $J = 1.3$ Hz) were characteristic for H_{17} and H_{18} , respectively.



Substance (II) — $C_{19}H_{26}O_7$, mp 188–190°C (ethanol), $[\alpha]_D^{20} -26^\circ$ (c 5.0; chloroform). From its IR, PMR, and ^{13}C NMR spectra and its physicochemical constants, substance (II) proved to be identical with the pseudoguaianolide britanin [4].

Only britanin has been isolated from this plant, by aqueous extraction [5].

In a concentration of $2 \cdot 10^{-6}$ M, britanin inhibited the germination of radish seeds by 87% of mustard by 85%, and of wild oats by 63%, and it completely suppressed the growth of

*Deceased.

Institute of Organic Synthesis and Coal Chemistry, Central Kazakhstan Branch, Academy of Sciences of the Kazakh SSR, Karaganda. Translated from *Khimiya Prirodnykh Soedinenii*, No. 6, pp. 797–798, November–December, 1984. Original article submitted September 22, 1983.