ARTAUSIN — A NEW SESQUITERPENE LACTONE FROM *Artemesia austriaca*

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The flower heads and leaves of *Artemesia austriaca* Jacg. (Austrian wormwood) collected in the following phase in the environs of Karaganda, Kazakh SSR, were exhaustively extracted with acetone (1:5). The concentrated extract was treated with 60% aqueous ethanol. The resulting precipitate was separated off, and the filtrate was treated with chloroform. The resin obtained after the evaporation of the chloroform was chromatographed on a column of KSK silica gel (1:30). On elution with benzene—ether (9:1, 4:1, and 1:1) and with ether, four crystalline substances were isolated.

Substance (I) — $C_{15}H_{20}O_3$, mp 139-141 C (ethanol). Yield 0.6% calculated on the air-dry raw material.

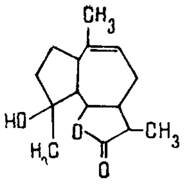
Substance (II) — $C_{15}H_{18}O_4$ H_2O, mp 149-150°C (ethanol). Yield 0.03%. From its physicochemical constants and its IR, UV, PMR, and ^{13}C NMR spectra and a comparison of them with literature information [1, 2], compounds (I) and (III) were identified as the sesquiterpene lactones arborescin and austricin, respectively.

Substance (III) — $C_{15}H_{22}O_3$, mp 201-204°C (ethanol) — proved to be a new sesquiterpene lactone and we have called it artausin. Yield 0.005%. Its IR spectrum had absorption bands at (cm^{-1}) 3470 (OH group), 1750 (carbonyl of a γ-lactone), and 1630 (>C=C<). The ^{13}C NMR spectrum (Bruker WR-80, 21.5 MHz, $CDCl_3$) showed the signals of 15 carbon atoms; three quartets, three triplets, six doublets, and three singlets.

When (III) was dehydrogenated over Se, chamazulene was obtained. These facts indicate the guaiane structure of the main skeleton of the lactone. The PMR spectrum of (III) (Bruker M-400, 400 MHz, $CDCl_3$, 0 — TMS) contained a doublet at 1.18 ppm (3 H, J = 6 Hz) of a methyl group at C-11, a singlet at 1.22 ppm (1 H) of the proton of a tertiary OH group, a quartet at 1.86 ppm (3 H, J = 1 Hz) characterizing the interaction of a methyl group at a double bond with H-9 and with protons at C-8, and a doublet of sextets at 2.64 ppm (1 H, J_{H_α,H_β} = 16 Hz) — H_β at C-8 (the sextet is formed through the interaction of $H_{8\beta}$ with C-10—CH_3, H-7, and H-9). When the signal of the olefinic proton was suppressed (double resonance), the signal at 2.64 ppm changed its multiplicity to a doublet of quintets. A multiplet at 3.20 ppm (1 H, $J_{6,7}$ = 11 Hz) was assigned to H-7.

The signal of the lactone proton appeared as a doublet of doublets at 4.15 ppm (1 H, $J_{6,7}$ = 11 Hz, $J_{5,6}$ = 9.5 Hz) characterizing the attachment of the lactone ring at C-6—C-7 [3, 4]. A multiplet in the 5.39 ppm region (1 H, the width of the signal at half-height of the intensity amounted to 6 Hz) corresponded to an olefinic proton (the splitting was due to its interaction with the 10-CH_3 group, H-1, and the protons at C-8).

Substance (III) was not acetylated by acetic anhydride and was not oxidized by chromium trioxide in pyridine, i.e., its hydroxy group was tertiary. On the basis of the results obtained and a comparison of them with literature information [3-5], we suggest for (III) the structure of 4-hydroxyguai-9(10)-en-6,12-olide as the most probable.



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Substance (IV) — $C_{18}H_{16}O_5$, mp 180-183°C (ethanol). Yield 0.007%. UV spectrum, $\lambda_{max}^{C_2H_5OH}$ nm: 244 (ε 15,200), 276 (ε 13,600), 342 (ε 19,200).

IR spectrum, ν_{max}^{KBr} cm^{-1}: 3600-3400 (—OH), 1670 (>C=O), 1630, 1590 (aromatic nucleus). From its physicochemical constants and spectral characteristics, (IV) was identified as 5-hydroxy-4',7-dimethoxy-6-flavone [6].

This is the first time that arborescin and 5-hydroxy 4',7-dimethoxy-6-methylflavone have been isolated from *Artemesia austriaca*.

The extraction of the epigeal part of *Artemesia austriaca* with hot water, followed by extraction with chloroform and chromatography of the resin so obtained on a column of KSK silica gel (1:20) yielded 0.11% of arborescin and 0.05% of austricin, calculated on the air-dry raw material.

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CARBONIZED CALCIUM HYDROMETASILICATE — A NEW EFFECTIVE ADSORBENT FOR THE SEPARATION OF NATURAL COMPOUNDS BY THIN-LAYER CHROMATOGRAPHY

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Carbonized calcium hydrometasilicate (KMK-20 — the numeral denotes the approximate percentage CO_2 content) is a surface-layer silicate material (the matrix being $CaSiO_3$ and the working surface $CaCO_3$; s ~ 200 m^2/g, V_{pore} ~ 0.9 cm^3/g, pH ~ 7.6, grain size 5-10 μm [1]). In its chromatographic activity, determined from the separation of a standard mixture of dyes (Fig. 1), KMK-20 is not inferior to adsorbents widely used in the TLC of natural compounds. Our aim was a study of the possibility of using KMK-20 for this purpose.

The results of a separation of a number of natural compounds on KSK silica gel, Silufol UV-254, and KMK-20 indicates its higher separating capacity and sensitivity. Thus, in the case of teucrins H1-H4, diterpene furolactones of the clerodane type (Fig. 2), the R_f values on KMK-20 were 13, 70, 40, and 60 (here and below, R_f 100), and on KSK silica gel they were 33, 68, 69, and 80. In the separation of the glycosides linarin and pectolinarin on KMK-20 it was possible to reveal an impurity component of the linarin which was not determined on Silufol UV-254 (Fig. 3). The aglycons of these glycosides — acacetin and pectolinarigenin — were separated on KMK-20 with R_f 35 and 83, and on Silufol UV-254 with R_f 51 and 56, respectively. A mixture of alkaloids was also readily separated on KMK-20: codeine, floripavine, fugapavine, and mecambridine — R_f 43, 55, 74, and 83, respectively (eluent: ethyl acetate—methanol—chloroform—water (7:2:1:1)). Methanolic extracts of the epigeal and radical parts of mullein were separated with the following R_f values: KMK-20 — 33, 36, 45, 51, 60, 64, 73*, 80*, 90 (epigeal part) and 51, 60, 65, 70, 75*, 81*, and 97 (radical part); Silufol UV-254 — 14, 29, 31, 34, 37, 40, 98, and 13, 29, 37, 42, and 97, respectively (* — spot detected only in TLC on KMK-20; eluent: ethyl acetate—methanol—chloroform—water (7:2:1:1)).

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