eluted a mixture of stereoisomeric cembra-7,11-dien-2-ols (yield 25%). Petroleum ether containing 12% of diethyl ether eluted 2-epiallylcembrol (8.5%) with n_D^{23} 1.5050, $[\alpha]_D^{23}$ −64.6° (c 8.1; chloroform); IR spectrum (in CCl_4) 3630, 1385, 1375, 1025 cm^{-1}; NMR spectrum (ppm): 1.52 and 1.55 (3H each, C_8-CH_3 and $C_{12}-CH_3$), 1.63 (3H, C_4-CH_3), 4.08 (1H, triplet, $J_{1,2} = J_{2,3} = 9.0$ Hz, H_2), 4.8-5.1 (2H, multiplet, H_7 and H_{11}), 5.15 (1H, doublet, $J_{2,3} = 9.0$ Hz, H_3). Petroleum ether containing 15% of diethyl ether eluted allylcembrol (I) (46%) with mp 37-38°C $[\alpha]_D^{21}$ +58.5° (c 6.14: chloroform); literature data: mp 37-38°C $[\alpha]_D$ +53° [2]; $[\alpha]_D$ +55.4° (c 2.06; chloroform) [1].

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HARPAGIDE AND HARPAGIDE ACETATE FROM SOME SPECIES OF THE FAMILY LABIATAE

N. F. Komissarenko, A. I. Derkach,
I. P. Sheremet, and D. A. Pakali

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It is known that some species of the family Labiatae contain iridoid compounds [1]. We have investigated a number of species of this family for their contents of harpagide and harpagide acetate: *Stachys iberica* Bieb., *St. balansae* Boiss et Ky., *St. spectabilis* Choisy, *St. fruticulosae*, Bieb., *St. grossheimii* Kapeller., *St. sylvatica* L., *St. lavandulifolia* Vahl., *St. germanica* L., *St. inflata* Benth., *St. atherocalyx* C. Koch., *Betonica macrantha* C. Koch., *B. nivea* Stev., *B. orientalis* L., *B. officinalis* L., *Ajuga reptaus* L.

By paper chromatography in the butan-1-ol−acetic acid−water (4 : 1 : 2) system, harpagide and harpagide acetate were detected in *St. iberica* Bieb., *St. atherocalyx* C. Koch., *Ajuga reptaus* L., *Betonica macrantha* C. Koch., *B. nivea* Stev., *B. orientalis* L., *B. officinalis* and harpagide in *St. spectabilis* Choisy., *St. fruticulosa* Bieb., *St. grossheimii* Kapeller., *St. lavandulifolia* Vahl., *St. sylvatica* L. When the chromatograms were treated with a 3% ethanolic solution of p-dimethylaminobenzaldehyde containing 1.5% of hydrochloric acid (Stahl's reagent) [2], they appeared in the form of deep blue spots with R_f 0.41 and 0.51, respectively.

The iridoids were isolated from the epigeal parts of the separate species in the following way: The comminuted raw material was treated with 80% ethanol, the extract was evaporated to an aqueous residue, and this was freed from chlorophyll and lipophilic substances with chloroform. To separate the flavonoids, the purified aqueous fraction of the extract was deposited on a column of polyamide sorbent and washed with water.

The combined iridoids free from flavonoids was separated on a column of polyamide sorbent with elution by chloroform and then mixtures of chloroform and ethanol with increasing concentrations of the latter. Two substances were isolated − harpagide acetate (R_f 0.51) and harpagide (R_f 0.41). The harpagide acetate was crystallized from a mixture of chloroform and ethanol (4 : 1) in the form of white acicular crystals with mp 153-155°C, $[\alpha]_D^{20}$ −111° (c 0.1; ethanol), $C_{17}H_{26}O_{10}$. On hydrolysis by the enzymes of the grape snail, it decomposes into D-glucose, acetic acid, and an aglycone which, as it separated out, colored the solution deep blue with a subsequent separation of a dark-colored precipitate.

To obtain the deacetyl derivative, the substance was saponified with 5% alcoholic caustic soda. A product $C_{15}H_{24}O_9$, $[\alpha]_D^{20}$ −133° (c 0.1; ethanol) was obtained which could not be crystallized.

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On the basis of the physicochemical properties of the initial substance, the products of its cleavage, and also results of parallel chromatography with an authentic sample of harpagide acetate obtained from V. I. Litvinenko [3], the iridoid isolated with R$_f$ 0.51 was identified as harpagide acetate.

Harpagide – a substance with R$_f$ 0.41 – was isolated in the form of a white amorphous powder with the empirical formula $C_{15}H_{24}O_9$, $[\alpha]^{20}_D - 136°$ (c 0.1; ethanol), which proved to be identical with the deacyl derivative obtained from harpagide acetate.

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ALANTOLACTONE FROM Inula grandis

S. A. Lugovskaya, N. V. Plekhanova,
and K. Yu. Orozbaev

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From fresh rosette leaves of Inula grandis Schrenk. [1, 2], collected on May 10, 1974 on the slopes of the foothills of the Khirgiz range, by extraction with chloroform followed by chromatography on alumina, from a petroleum ether–benzene (7 : 3) fraction we have isolated a substance (I) with mp 76-78°C. IR spectrum: 1754 cm^{-1} (γ-lactone), 1645, 893, 885, and 813 cm^{-1} ($>C=CH_2$), and 862 cm^{-1} ($-CH=C<$). NMR spectrum (ppm): doublets at 6.04 and 5.48 (J = 2 Hz) (exocyclic methylene on a lactone ring); 5.00 (J = 4 Hz) (H-8 lactone proton); singlet at 3.43 (proton in the vicinal position to a lactone; H-7); singlet at 1.10 (3H, methyl at C_{10}); doublet at 1.00 ppm (J = 7 Hz, methyl at C_4).

Substance (I) has also been isolated from the rosette leaves of Inula grandis cultivated in the botanical gardens of the Academy of Sciences of the Khirgiz SSR.

From the roots of Inula grandis in the fruit-bearing stage (5-yr growth) cultivated in the botanical garden we have isolated a substance (II) with mp 113-115°C. IR spectrum (cm^{-1}): 1770 (γ-lactone), 1645, 890 ($>C=CH_2$), 826 ($>C=CH_2$). NMR spectrum (ppm): doublets at 5.96 and 5.45 (J = 1.5 Hz) and 4.62 and 4.30 (J = 2 Hz) (exocyclic methylene groups on a lactone ring), multiplet at 4.40 (h-8 lactone proton), sextet with its center at 2.82 (J Σ = 32 Hz) (H), singlet at 0.75 (3H, methyl at C_{10}).

The results of a comparison of the physicochemical properties with literature information permitted the assumption that substance (I) is alantolactone and (II) isoalantolactone [3-8].

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