

methanol (20:1) system gave the crystalline 28- $\alpha$ -L-rhamnoside of ursolic acid 3-O-acetate (V):  $C_{38}H_{60}O_8$ ; mp 158-164°C (from methanol),  $[\alpha]_D^{22} +19.3 \pm 2^\circ$  (s 1.03; pyridine).  $\nu_{\text{KBr}}^{\text{max}}$ ,  $\text{cm}^{-1}$ : 3550-3350 (OH); 1742 (C=O groups); 1255 (ester grouping). PMR ( $C_5D_5N$ , ppm): 0.71, 0.77, 1.01 ( $7 \times \text{CH}_3$  methyl protons at C-23, C-24, C-25, C-26, C-27, C-29, and C-30, s); 1.54 (methyl group of the rhamnose residue, d,  $J = 5.5$  Hz); 1.91 (3H of the Ac group at C-3, s); 4.04-4.64 (proton at C-3 and the protons of all the carbon atoms of the rhamnose residue apart from C-1' and C-6', m); 5.28 (H at C-12, m); 6.57 (anomeric proton of the rhamnose residue, br.s). The yield of product (V) was 77.6%, calculated on the ursolic acid 3-acetate.

The configurations of the glycosidic bonds in compounds (II), (III), and (V) were determined from molecular rotation differences [3].

The PMR spectra were taken on a JNM-4H-100 (100 MHz) instrument (HMDS,  $\delta$  scale).

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#### CARDIAC GLYCOSIDES OF *Erysimum pulchellum*

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*Erysimum pulchellum* (Willd) J. Gay (rockery erysimum), family Brassicaceae, is an herbaceous plant growing in Asia Minor and the southern Transcaucasus [1]. We have found no information of the cardenolide composition of this plant. We investigated the epigeal part of rockery erysimum grown and collected in the flowering stage in 1986 in the nursery of the All-Union Scientific-Research Institute of Medicinal Plants. The ground raw material was exhaustively extracted with 80% ethanol, and the extract was concentrated in vacuum to an aqueous residue. Then 96% of ethanol was added to create a final ethanol concentration of about 25%. The solution was filtered through alumina, which separated off the chlorophylls and resins and the bulk of the phenolic compounds. The cardenolides were extracted from the filtrate with chloroform, and then with chloroform-ethanol (2:1). The extracts were evaporated.

Analysis of the product obtained with the aid of paper chromatography and chromatography on Silufol in various solvent systems showed that it contained not less than ten cardenolides. The mixture of substances was separated by chromatography on silica gel using ethyl acetate-methanol mixtures of increasing polarity as eluents. Five cardenolides were isolated in the individual state, including erysimoside, bipindogulomethyloside, erysimin, and strophantidin (for their structures, see [2]). The cardenolides were identified by their properties, IR spectra, and the results of paper chromatography in comparison with authentic samples.

Erysimoside, mp 170-174/235-240°C; yield 0.055%.

Bipindogulomethyloside, mp 153-156°C,  $[\alpha]_D^{20} -16 \pm 3^\circ$  (c 0.3; methanol) yield 0.08%.

Erysimin, mp 152-155/175-178°C; yield 0.006%.

Strophantidin, mp 224-230°C. The presence of the free aglycon strophantidin gave grounds for assuming that this plant may contain glucostrophantidin. In actual fact, in the other glycosides, not isolated in the pure form, there was one chromatographically identical with a sample of glucostrophantidin.

The fifth cardenolide, having  $[\alpha]_D^{20} -43 \pm 5^\circ$  (c 0.4; methanol) was, apparently, a new cardiac glycoside. Its structure is being established.

Erycordin was also detected chromatographically.

A feature of rockery erysimum is that neither erysimoside nor erysimin is the main glycoside, as in the majority of Erysimum species. In rockery erysimum, bipindogulomethyloside predominates, and in this respect it is closer to the genus Cheiranthus than to Erysimum. The synonym of rockery erysimum, Cheiranthus pulchellus Willd, is apparently not fortuitous.

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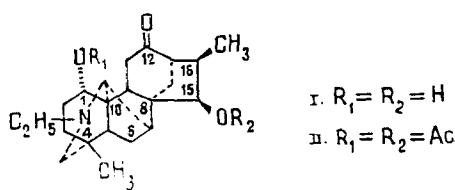
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#### DIHYDROSONGORINE FROM THE EPIGEAL PART OF *Aconitum karacolicum*

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Continuing the separation of the total alkaloids of the epigeal part of Aconitum karacolicum Rapaics., collected in the valley of the R. Irisu (KirgSSR) [1], we have isolated a base with the composition  $C_{22}H_{33}NO_3$  (I), mp 202-204°C (ethanol). The IR spectrum of the alkaloid had the absorption bands of hydroxy groups at  $3400-3500 \text{ cm}^{-1}$  and of a carbonyl group in a six-membered ring at  $1700 \text{ cm}^{-1}$ . The PMR spectrum ( $CDCl_3$ ,  $\delta$  scale), showed signals from a N-ethyl group (1.00 ppm, 3 H, triplet,  $J = 7 \text{ Hz}$ ), from a tertiary C-methyl group (0.68 ppm, singlet), and from a secondary methyl group (0.74 ppm, 3H, doublets  $J = 7 \text{ Hz}$ ). The mass spectrum of the alkaloid was close to those of bases of the songorine group [2]. When the alkaloid was acetylated with acetic anhydride in the presence of pyridine, a diacetate derivative (II) was obtained with mp 128-130°C (petroleum ether), the PMR spectrum of which showed the signals of a secondary methyl group (0.63 ppm, 3H, d,  $J = 7 \text{ Hz}$ ), a tertiary C-methyl group (0.68 ppm, 3H, s), a N-ethyl group (1.00 ppm, 3H, t,  $J = 7 \text{ Hz}$ ), and also a one-proton quartet at 4.97 ppm (H-1 $\alpha$ ) [3] and a one-proton doublet at 5.12 ppm ( $J = 8 \text{ Hz}$ ). Consequently, the developed formula of the base is:  $C_{15}H_{19}(>N-C_2H_5)(\bigtriangleup C-CH_3)(>HC-CH_3)(>C=O)(OH)_2$ . A comparison of the developed formulas of (I) and of songorine showed that in (I) there was a secondary methyl group in place of the terminal methylene group in songorine. These facts indicated that the alkaloid (I) was dihydrosongorine, which has been obtained previously by the catalytic hydrogenation of songorine [2, 4]. In actual fact, a comparison of the constants and also of mass and IR spectra showed their identity. It must be mentioned that the configuration of the secondary methyl group at C-16 in dihydrosongorine had remained unelucidated. Analysis of the PMR spectrum of dihydrosongorine diacetate permitted the conclusion that this methyl group is  $\beta$ -oriented. As already mentioned, in the PMR spectrum of (II), in addition to the H-1 $\alpha$  signal, there is a one-proton doublet at 5.12 ppm with a splitting constant of 8 Hz which is obviously due to the H-15 $\alpha$  atom at an acetoxy group. A study of a model of dihydrosongorine showed that the dihedral angle between the  $\alpha$ -proton at C-15 and the  $\beta$ -proton at C-16 is  $110-120^\circ$  ( $J_{\text{calc}} = 2.5 \text{ Hz}$ ), and that with the  $\alpha$ -proton at C-16 is  $10-20^\circ$  ( $J_{\text{calc}} = 8.5 \text{ Hz}$ ). The observed splitting constant agrees well with the  $\beta$ -configuration of the methyl group at C-16, and, consequently, the structure of dihydrosongorine can be represented by formula (I).



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