this region that the zones of the acids isomerizable to abietic acid are found. The absence in the TLC of tall-oil rosin of spots in this R_f interval indicates the absence or insignificant presence of these acids. This result agrees completely with the conclusions of Maslennikov, et al.[6], that the isomerization of tall-oil rosin does not increase the abietic acid content.

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RHAMNOSIDES OF GLYCYRRHETIC AND URSOLIC ACIDS

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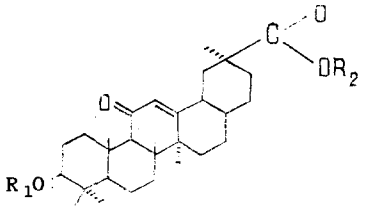
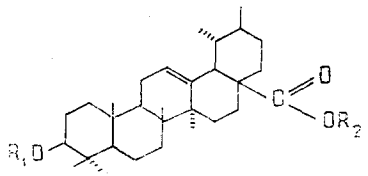
The glycosylation of glycyrrhetic acid (I) and of ursolic acid 3-acetate (VI) with acetobromorhamnose has been carried out under the conditions given in the literature [1, 2]. The glycoside acetates so obtained are saponified with a methanolic solution of sodium methanolate.

The products of the interaction of glycyrrhetic acid with acetobromorhamnose, after partial deacetylation, were chromatographed on a column of SiO_2. As a result of elution with the chloroform–methanol (50:1) system, the crystalline 30-α-L-rhamnopyranoside of glycyrrhetic acid 3-acetate (II) was obtained: $C_{38}H_{58}O_9$, mp 186-194°C (from methanol); $[\alpha]_D^{22}$ +86.4 ± 2° (c 1.0; pyridine); ν_{max}^{KBr}, cm^{-1}: 3550-3300 (OH); 1745, 1735, 1660, (C=O groups); 1255 (ester grouping).





I. $R_1 = R_2 = H$
II. $R_1 = Ac$; $R_2 = \alpha$-L-Rha
III. $R_1 = R_2 = \alpha$-L-Rha
IV. $R_1 = Ac$; $R_2 = H$
V. $R_1 = Ac$; $R_2 = \alpha$-L-Rha

On further elution with the chloroform–methanol (10:1) system, the crystalline 3,30-di-α-L-rhamnoside of glycyrrhetic acid (III) was obtained: $C_{42}H_{66}O_{12}$; mp 231-237°C (from methanol; $[\alpha]_D^{22}$ +59.1 ± 2° (c 0.94; pyridine); ν_{max}^{KBr}, cm^{-1}: 3550-3200 (OH); 1745, 1662 (C=O groups). PMR (C_5D_5N, ppm): 0.66, 0.75, 0.85, 0.98, 1.07, 1.16, 1.27 (7 × CH_3, methyl protons at C-23, C-24, C-25, C-26, C-27, C-28, and C-29, s); 1.53 (6H, methyl groups of two rhamnose residues, d); 3.90-4.80 (8H on all the carbon atoms of the two rhamnose residues apart from the first and sixth, m); 5.16 (anomeric rhamnose proton at C-3, br.s.); 5.79 (H at C-12, s); 6.63 (anomeric rhamnose proton at C 30, br.s). The yield of product (III) was 40%, calculated on the initial glycyrrhetic acid (I).

The products of the interaction of ursolic acid 3-acetate (IV) with acetobromorhamnose, after deacetylation, were chromatographed on a column of SiO_2. Elution with the chloroform–

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methanol (20:1) system gave the crystalline 28-α-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 ± 2° (s 1.03; pyridine). ν_{max}^{KBr}, cm^{-1}: 3550-3350 (OH); 1742 (C=O groups); 1255 (ester grouping). PMR (C_5D_5N, ppm): 0.71, 0.77, 1.01 (7 × 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, δ 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 an 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 strophanthidin (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 ± 3° (c 0.3; methanol) yield 0.08%.

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

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

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