The ethereal solution was separated into acidic, phenolic, and lactone fractions. The acidic fraction was chromatographed on KSK silica gel. On elution with ether, acicular crystals with mp 201–202° C deposited which, on the basis of their IR spectrum, R_f value, and a mixed melting point were identified as the coumarin scopoletin. Then the unsaponifiable neutral fraction was chromatographed on alumina. From a methanolic eluate we isolated a substance with the composition $C_{29}H_{50}O$, mp 139–140° C (from acetone), which gave the Liebermann-Burchard reaction for sterols.

By comparing the IR spectra and R_f values and by means of a mixed melting point test the substance was identified as β-sitosterol. Scopoletin and β-sitosterol have not previously been found in Artemisia dracunculus.

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FLAVONOIDS OF ARMORACIA RUSTICANA AND BARBAREA ARCUATA

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In the epigeal parts of Armoracia rusticana Gaerth. Mey et Scherb. and Barbarea arcuata Rchb. by one-dimensional and two-dimensional paper chromatography and qualitative reactions [1] we have detected not less than five and eight flavonoid substances, respectively. The total flavonoids were separated on a column of Kapron. On elution with aqueous methanol, methanol, and mixtures of chloroform and methanol and of acetone and water, two individual compounds were isolated from the leaves of A. rusticana (X-1 and X-2) and three from the flower clusters of B. arcuata (C-1, C-2, C-3).

As a result of alkaline cleavage and acidic and enzymatic hydrolysis and the features of the IR and UV spectra with ionizing and complex-forming reagents [2–4], X-1, with mp 275–277° C was identified as kaempferol, X-2 with mp 311–313° C as quercetin, C-1 with mp 306–309° C as isorhamnetin, C-2 with mp 166–170° C as isorhamnetin 3-β-D-glucopyranoside, and C-3 provisionally as isorhamnetin 3-β-D-glycosyl-6-β-D-glucoside.

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PHENOLIC COMPOUNDS OF RHODODENDRON LUTEUM

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We have previously reported the isolation from Rhododendron luteum Sweet (pontic azalea) growing in the Ukrainian Poles'e the flavonoids quercetin, hyperoside, and avicularin [1]. From the same species growing in the Caucasus myricitrin

and azaleanthin have been isolated, in addition to quercetin, hyperoside, and avicularin [2].

The present paper gives the results of a further study of the phenolic compounds of the species mentioned.

The extract obtained from the leaves with 80% ethanol was evaporated to an aqueous residue and the latter was purified with benzene–chloroform (8 : 2). The purified aqueous residue was treated with ethyl acetate. The extract was evaporated and the residue was separated on a column of Kapron powder.

Elution with chloroform containing up to 5% of ethanol yielded a substance $C_{10}H_8O_4$ with mp 204–205° C fluorescing bright blue which crystallized from chloroform containing a small amount of ethanol. The substance was methylated ($C_{11}H_{10}O_4$, mp 144–146° C) and acetylated ($C_{12}H_{10}O_5$, mp 176–177° C).

The initial substance was identified with the hydroxycoumarin scopoletin [3] by its physicochemical properties, its methyl and acetyl derivatives, its UV and IR spectra, and its R_f values in various systems, and also by a mixed melting point.

Further elution with a gradual increase in the concentration of ethanol in the chloroform up to 25% permitted the isolation of a glycoside of a simple phenol and six flavonols (I–VI), three of which [quercetin (II), avicularin (IV), and hyperoside (V)] we have isolated previously from this plant [1].

The phenol glycoside, which had the empirical formula $C_{12}H_{16}O_7$, mp 147–148° C $[\alpha]_D^{19}$ −59.5° (methanol), gave a red color with diazotized sulfanilic acid. The substance underwent acetylation, forming a pentaacetyl derivative [$C_{22}H_{26}O_{12}$, mp 146 ° C, $[\alpha]_D^{19}$ −28° (acetone)] and was readily cleaved by 4% sulfuric acid and the enzymes of the fungus Aspergillus oryzae into d-glucose and hydroquinone. From its reaction product, IR spectra, R_f values, and mixed melting point it is identical with arbutin.

The flavonol I ($C_{15}H_{10}O_6$, mp 271–274° C) fluoresced yellow in filtered UV light, and gave a tetraacetate ($C_{23}H_{18}O_{10}$, mp 178–180° C). By means of the UV spectroscopy with ionizing and complex-forming reagents the substance was found to contain OH groups in positions 3, 5, 7, and 4'. It is known that such an arrangement of hydroxyls is observed in kaempferol. A comparison of various properties of the substance isolated and kaempferol showed their identity. The flavonols III ($C_{15}H_{10}O_8$; begins to sublime at 335° C and melts with decomposition at 344–350° C) and VI [$C_{21}H_{20}O_{12}$, mp 187–189° C, $[\alpha]_D^{19}$ −140° (ethanol)] were identical with myricetin and myricetin 3-O-α-L-rhamnoside, this identification being carried out as described previously [4].

The paper chromatography of an extract from the leaves of pontic azalea in the butan-1-ol–acetic acid–water (4 : 1 : 2) and 5% acetic acid systems with the parallel chromatography of authentic samples showed the presence of ferulic and feruloylquinic acids.

This is the first time that a coumarin derivative, scopoletin, and a flavonol, kaempferol, have been isolated from the genus Rhododendron L.

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