Substance (III): white crystals, mp 254°C. UV spectra $\lambda_{max}^{CH_3OH}$, nm: 261, 300 sh; CH_3COONa: $\Delta\lambda$ +0; H_3BO_3 + CH_3COONa: $\Delta\lambda$ +0; $AlCl_3$: $\Delta\lambda$ + 11; $AlCl_3$ + HCl: $\Delta\lambda$ +11; C_2H_5ONa: $\Delta\lambda$ +10. On hydrolysis with 10% H_2SO_4 (5 h), genistein, R_f 0.94 (system 2) and D-glucose, R_f 0.16 (system 1), were formed. Compound (III) gave no depression of the melting point in admixture with an authentic sample of genistin.

Substance (III) was identified as genistin (genistein 7-glucoside).

Substance (IV): colorless acicular crystals with mp 292°C, R_f 0.94 (system 2). UV spectra: $\lambda_{max}^{CH_3OH}$, nm: 263, 325; CH_3COONa: $\Delta\lambda$+10; H_3BO_3+CH_3COONa: $\Delta\lambda$+0; $AlCl_3$: $\Delta\lambda$+11; $AlCl_3$+HCl: $\Delta\lambda$+12; C_2H_5ONa: $\Delta\lambda$+15. A mixture with an authentic sample of genistein gave no depression of the melting point.

The experimental results obtained permit substance (IV) to be characterized as genistein (4',5,7-trihydroxyisoflavone).

Substance (V): colorless crystals, mp 297°C, R_f 0.88 (system 1), UV spectra: $\lambda_{max}^{CH_3OH}$, nm: 257, 282 sh. Compound (V) gave no depression of the melting point in admixture with 5-methylgenistein and can be identified as the latter.

We are the first to have detected the isoflavones formononetin and genistein and their glycosides ononin and genistin in weavers' broom; 5-methylgenistein has been isolated previously [2].

LITERATURE CITED

1. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
2. R. R. Paris and G. Faugeras, C.R., 261, No. 7, 1761 (1965).

FLAVONOIDS OF *Gentiana barbata*

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In order to find biologically active substances, we have studied the flavonoid composition of the epigeal part of *Gentiana barbata* collected in the Kizhinga region of the Buryat ASSR in July, 1977.

An ethyl acetate solution of the evaporated ethanolic extract was subjected to chromatographic separation on a column of silica gel, the substances being eluted with chloroform and mixtures of chloroform and methanol with increasing concentrations of the latter. Three substances of flavonoid nature (A, B, and D) were isolated. One more substance (C) was isolated from a chloroform extract. Compounds (A-D) were identified on the basis of the results of NMR, IR, and UV spectroscopy with ionizing and complex-forming additives (I), melting points, and chromatographic behavior with authentic samples.

Substance A, composition $C_{15}H_{10}O_5$, mp >300°C, λ_{max}^{MeOH} 270, 340 nm, M^+ 270 and substance B, with the composition $C_{15}H_{10}O_6$, mp >300°C, λ_{max}^{MeOH} 254, 270 sh, 300 sh, 350 nm, M^+ 286, were identified as apigenin and luteolin.

Substance C, with the composition $C_{16}H_{12}O_6$, mp 265-267°C, λ_{max}^{MeOH} 254, 272, 300 sh, 350 nm, M^+ 300, differed from substance B by the presence of a methoxy group, as can be seen from the NMR spectrum: singlet at 4.1 ppm (3 H) in trifluoroacetic acid (TFA). The position of the methoxy group was established on the basis of the UV spectra. In the presence of sodium methanolate, a bathochromic shift of the maximum of the long-wave band by 40 nm was observed, indicating the presence of a free 4'-OH group. In the presence of boric acid

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and sodium acetate, in contrast to substance B, no bathochromic shift of the maximum of the long-wave band was observed, which shows the presence of a methoxy group in position 3.

Substance C was identified as chrysoeriol — 4',5,7-trihydroxy-3'-methoxyflavone [2].

Substance D had the composition $C_{22}H_{22}O_{10}$, mp 244-245°C, λ_{max}^{MeOH} 270, 330 nm, and was a glycoside. Its hydrolysis gave an aglycone of the composition $C_{16}H_{12}O_5$, which was identified as acacetin with a known sample.

NMR spectrum (TFA, δ, ppm): 8.22 (d, J = 8 Hz, H-2',6'), 7.38 (d, J = 8 Hz, H-3',5'), 7.28 (d, J = 2.5 Hz, H-6), 7.10 (d, J = 2.5 Hz, H-8), 5.56 (d, J = 7 Hz, proton of the glycosidic center of β-glucose), 4.08 (s, $-OCH_3$), 3.8-4.4 (signals of glucose protons). The carbohydrate part of substance D, consisting of glucose, was attached in position 7 of the acacetin. The UV spectrum of the substance had a bathochromic shift of the maxima in the presence of $AlCl_3$, which was not observed on the addition of sodium acetate. Thus, substance D has the structure of 7-O-β-D-glucopyranosyloxy-5-hydroxy-4'-methoxylflavone — tilianin [3].

LITERATURE CITED

1. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
2. A. Lovecy et al., J. Chem. Soc., 817 (1930).
3. T. A. Geissman, The Chemistry of Flavonoid Compounds, Pergamon, Oxford (1962).

PHENOLIC COMPOUNDS OF Rhodiola gelida

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We have investigated the composition of the phenolic components of Rhodiola gelida Schrenk. collected in the Frunze province of the Kirghiz SSR. For their isolation, 1 kg of the comminuted rhizomes with roots was extracted with 70% ethanol and the extracts were concentrated in an aqueous residue which was treated with chloroform and ethyl acetate. Concentration of the chloroform extract yielded substance (I), which was identified as p-hydroxyacetophenone [1]. The ethyl acetate extract was separated on a column of Kapron. Elution with water gave substances (II) and (III), and aqueous ethanol, followed by rechromatography in the chloroform—ethanol (3:2 and 2:3) systems, gave substances (IV) and (V).

Substance (II), $C_8H_{10}O_2$, mp 92-93°C. Substance III, $C_{14}H_{20}O_7$, mp 158.5-160°C, $[\alpha]_D^{20}$ −31° (c 2.0, H_2O), λ_{max} 221, 275 nm, PC R_f 0.81 (II), 0.46 (III) (2% acetic acid). The quantitative acidic and enzymatic hydrolyses of substance (III) yielded (II) and D-glucose. From the results of UV and IR spectroscopy, qualitative reactions, and the absence of a depression of the melting point of mixtures with authentic samples, the compounds were identified as 4-hydroxy-β-phenylethanol (p-tyrosol) and its glucoside (salidroside) which have been detected previously in other species of Rhodiola [2, 3].

Substance (IV), $C_{21}H_{20}O_{12}$, mp 204-205°C, $[\alpha]_D^{20}$ −29° (c 0.2; methanol), $\lambda_{max}^{CH_3OH}$ 275, 334 375 nm, $\nu_{C=O}$ 1660 cm^{-1}, R_f 0.11 and 0.65 (here and below, 15 and 60% acetic acid).

Substance (V), $C_{20}H_{18}O_{11}$, mp 242-244°C, $\lambda_{max}^{CH_3OH}$ 277, 280, 326, 385 nm, $\nu_{C=O}$ 1665 cm^{-1}, R_f 0.18 and 0.86. On acid and enzymatic hydrolysis with β-hydrolases the two compounds gave a single aglycone, which was identified as herbacetin (3,4',5,7,8-pentahydroxyflavone), and equimolar amounts of sugars: in substance (IV) the herbacetin was glycosylated with D-glucose and in (V) with L-arabinose.

The glycosides possessed a yellow fluorescence in UV light and gave a positive gossypetone test, which shows the presence of 3-OH and 5,8-dihydroxy groupings. From UV spectra with complex-forming and ionizing reagents [4], free hydroxy groups were found in positions 3,5,7, and 8 of substance (IV) and at C_3, C_5, C_8, and C_4', in substance (V).

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