Substances (V) and (VI) were characterized as quercetin and luteolin. After an ethyl-acetate fraction had been obtained, the extract was treated with n-butanol. From the combined butanolic extracts, likewise, a mixture of substance containing mainly (VII) and (VIII) was isolated. They were identified by paper chromatography in the presence of markers as orientin and vitexin. The investigations are proceeding.

LITERATURE CITED

1. L. K. Klyshev, V. A. Bandyukova, and L. S. Alyukina, Flavonoids of the Plants of Alma-Ata [in Russian] (1978).
2. M. Jau, P. Lebreton, and R. Letoublon, Boissiera, 19, 219 (1971).
3. J. Tronchet, Ann. Sci. Univ. Besancon. Bot., No. 15, 47 (1974).
4. L. Hörhammer, H. Wagner, and S. Dhingra, Naturwissenschaften, 45, No. 1, 13 (1958).

FLAVONOIDS OF *Spartium junceum*.

II. ISOFLAVONES

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By the two-dimensional paper chromatography of ethanolic extracts of the epigeal part of *Spartium junceum* L. (weavers' broom) collected in the flowering phase we have detected the presence of a series of substances belonging, according to their chemical and physicochemical characteristics, to the classes of isoflavones and their glycosides. For the preparative isolation of these compounds we used column and thin-layer chromatography. The following substances were detected and identified.

Substance (I): white plates, mp 213°C, soluble in methanol and ethanol and, more sparingly, in ethyl ether, R_f 0.61 and 0.74 [here and below, system (1) butan-1-ol—glacial acetic acid—water (4:1:5), and system (2) 15% acetic acid]. UV spectra $\lambda_{max}^{CH_3OH}$, nm: 260, 300 sh. The absence of a bathochromic shift of the absorption maximum on the addition of CH_3COONa ($\Delta\lambda$ +0 nm) and the appearance of a bathochromic shift ($\Delta\lambda$ +8 nm) in the aglycone after acid hydrolysis showed that the sugar component of substance (I) was present in the C_7 position. The small bathochromic shift of the absorption maximum of the aglycone in the presence of sodium ethanolate ($\Delta\lambda$ +9 nm) and the absence of a shift with $AlCl_3$ confirmed that the C_5 position lacked a hydroxy group and a hydroxy group at C_4' was substituted [1].

Hydrolysis with 10% H_2SO_4 (5 h) formed the aglycone formononetin, R_f 0.92 and 0.32 (systems 1 and 2, respectively), the melting points of the acetate (168°C) and methyl derivatives (157°C) of which coincided with those of the corresponding derivatives of an authentic sample of formononetin. In the hydrolysate, D-glucose was detected by paper chromatography, with R_f 0.17 (system 1). The results of enzymatic hydrolysis (*Aspergillus oryzae*) permit the assumption that the carbohydrate component is attached to the aglycone by a β-glycosidic bond.

On the basis of the results obtained, it may be concluded that substance (I) is ononin (formononetin 7-O-β-glucopyranoside).

Substance (II): white crystals with mp 256°C, soluble in methanol, ethanol, and diethyl ether, R_f 0.93 and 0.38 (systems 1 and 2, respectively). UV spectra $\lambda_{max}^{CH_3OH}$, nm: 250, 300 sh; CH_3COONa: $\Delta\lambda$ +8; H_3BO_3 + CH_3COONa: $\Delta\lambda$ +6; $AlCl_3$: $\Delta\lambda$ +0; $AlCl_3$ + HCl; $\Delta\lambda$ −1; C_2H_5ONa: $\Delta\lambda$ +8. A mixture of substance (II) with synthetic formononetin gave no depression of the melting point.

Substance (II) is formononetin (7-hydroxy-4'-methoxyisoflavone).

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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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