FLAVONOIDS OF *Spartium junceum*.

I. FLAVONES AND FLAVONOLS

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We have investigated the epigeal part of *Spartium junceum* L. (weavers' broom), family Fabaceae collected in July, 1978 in the Yalta region.

There is information in the literature that the epigeal part of this plant contains flavone C-glycosides [1, 2] and O-glycosides of quercetin [3] and of luteolin [4].

By two-dimensional paper chromatography [here and below: system (1) butan-1-ol—glacial acetic acid—water (4:1:5) and system (2) 15% acetic acid] of ethanolic extracts from the epigeal part of the plant we detected not less than 15 substances of polyphenolic nature belonging to the classes of flavones, flavonols, and isoflavones.

By extracting 1 kg of air-dry raw material with 70% ethanol followed by concentration, purification with chloroform, and extraction of the polyphenolic compound with ethyl acetate, we obtained 5 g of total material. By column chromatography, from this total material we isolated six substances belonging to the classes of flavones and flavonols and their glycosides.

The structures of the compounds isolated were shown by the use of chemical and physicochemical methods.

Substance (I) formed light yellow crystals with mp 190°C readily soluble in aqueous solutions of methanol and ethanol, R_f 0.43 and 0.51 (systems 1 and 2, respectively). UV spectra: $\lambda_{max}^{CH_3OH}$, nm: 256, 264 sh, 354; CH_3COONa; $\Delta\lambda$ + 26; H_3BO_3 + CH_3COONa: $\Delta\lambda$ + 25; $AlCl_3$: $\Delta\lambda$ + 40; $AlCl_3$ + HCl: $\Delta\lambda$ + 27; C_2H_5ONa: $\Delta\lambda$ + 37. On hydrolysis with 1% H_2SO_4 (30 min) the aglycone quercetin and the sugar component rutinose were formed, and on hydrolysis with 3% H_2SO_4 (3 h), quercetin, D-glucose and L-rhamnose. A mixture with an authentic sample of rutin isolated from buds of the Japanese pagoda tree gave no depression of the melting point.

On the basis of the results obtained it was established that the substance was rutin (quercetin 3-O-[O-β-L-rhamnopyranosyl-(1 → 6)-α-D-glucopyranoside]).

Substance (II) formed yellow acicular crystals with mp 240°C, readily soluble in dilute methanol and dilute ethanol, R_f 0.37 and 0.57 (systems 1 and 2, respectively). UV spectra: $\lambda_{max}^{CH_3OH}$, nm: 255, 265 sh, 362; CH_3COONa: $\Delta\lambda$+17; H_3BO_3+CH_3COONa: $\Delta\lambda$+11; $AlCl_3$: $\Delta\lambda$+33; $AlCl_3$ + HCl: $\Delta\lambda$+20; C_2H_5ONa: $\Delta\lambda$+31. On enzymatic hydrolysis with emulsin, quercetin and D-glucose were detected.

The substance was identified as isoquercitrin (quercetin 3-O-β-D-glucopyranoside).

Substance (III) formed yellow crystals with mp 211°C, R_f 0.49 (system 1). UV spectra: $\lambda_{max}^{CH_3OH}$, nm: 265, 365. Hydrolysis with 3% H_2SO_4 (3 h) led to quercetin and D-glucose. The substance gave no depression of the melting point in admixture with an authentic sample of spiraeoside isolated from the onion.

The experimental facts permit us to characterize the substance as spiraeoside (quercetin 4'-glucoside).

Substance (IV) formed light yellow crystals with mp 258°C readily soluble in aqueous solutions of methanol and of ethanol, R_f 0.44 and 0.16 [systems (1) and (2), respectively]. UV spectra: $\lambda_{max}^{CH_3OH}$, nm: 255, 267 sh, 348; CH_3COONa; $\Delta\lambda$+0; H_3BO_3+COONa: $\Delta\lambda$ +14; $AlCl_3$: $\Delta\lambda$ +50; $AlCl_3$ +HCl: $\Delta\lambda$+26; C_2H_5ONa: $\Delta\lambda$+29. Luteolin and D-glucose were found in the products of acid hydrolysis. The substance gave no depression of the melting point with an authentic sample of luteolin 7-glucoside.

According to the results obtained, the substance was luteolin 7-glucoside.

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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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