FLAVONES OF *Prunella vulgaris*

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UDC 633.88:582.675.1:
615.43

In a study of the study of the chemical composition of the epigeal part of *Prunella vulgaris* L. (family Lamiaceae) collected in July, 1985, in the environs of Tomsk, by two-dimensional and one-dimensional paper chromatography (in systems 1) 15% acetic acid and 2) butan-1-ol–acetic acid–water (4:1:5)) we detected substances of flavonoid nature. In order to isolate them, the defatted raw material was exhaustively extracted with 80% ethanol, the ethanolic extract was evaporated in vacuum to minimum volume and was diluted with water (1:2), and the purified aqueous extract was saturated with chloroform. After 20 h, a precipitate of substance C [1] crystallized out at the chloroform–water boundary.

The aqueous residue containing the sum of the phenolic compounds was transferred to a column of Woelm polyamide sorbent which was washed with water and with ethanol in weak concentrations (10 and 20%) until the reaction for hydroxycinnamic acids was negative. When the concentration of ethanol was raised (50 and 95%), substances A and B [2], were found in the eluates.

The fractions obtained were purified by repeated desorption on Silufol and polyamide plates. The flavonoids isolated were identified from their physicochemical constants, their hydrolysis products, and bathochromism.

Substance A – mp 328-330°C, R_f 0.06 (system 1), 0.56 (system 2), UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 351, 267, 256 nm; $\lambda_{max}^{C_2H_5ONA}$ 405, 268 nm; $\lambda_{max}^{CH_3COONa}$ 378, 270 nm; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 369, 258 nm; $\lambda_{max}^{AlCl_3}$ 401, 267 nm, $\lambda_{max}^{AlCl_3 + CHl}$ 362, 277, 260 nm;

Substance B – mp 234-237°C, $[\alpha]_D^{20}$ + 30.1° (s 0.6; methanol); R_f 0.29 (system 1), 0.37 (system 2). UV spectrum: λ_{max} C_2H_5OH 351, 270, 258 nm; λ_{max} C_2H_5ONa 410, 279 nm; $\lambda_{max}^{CH_3COONa}$ 390, 278 nm; $\lambda_{max}^{CH_3COONa + H_3BO_3}$ 376, 273 nm; $\lambda_{max}^{AlCl_3}$ 394, 279 nm: $\lambda_{max}^{AlCl_3 + HCl}$ 372, 278 nm.

Substance C – 256-258°C, $[\alpha]_D^{20}$ – 76.9° (s, 0.1; methanol); R, 011 (system 1), 0.40 (system 2). UV spectrum: λ_{max} C_2H_5OH 350, 257 nm; λ_{max} C_2H_5ONa 403, 391 276 nm; λ_{max} CH_3COONa 350, 282, 255 nm; λ_{max} $CH_3COONa + H_3BO_3$ 362, 261 nm; λ_{max} $AlCl_3$ 404, 270 nm; λ_{max} $AlCl_3$+HCl 382, 270 nm.

When substance B was heated in 10% H_2SO_4 solution it formed an isomer with the low R_f values of 0.14 (system 1) and 0.33 (system 2), which is characteristic for 6-C-glycosides. Under such conditions, substance C was split in 6 h into luteolin and D-glucose. The acid hydrolysis of substance B by Kihani's method gave an aglycon with R_f 0.56 (system 2), which permitted it to be assigned to luteolin. The carbohydrate moiety consisted of D-glucose with a trace of D-arabinose, the formation of the latter being characteristic for the hydrolysis of C-glycosides [3, 4].

On the basis of the results obtained, the flavonoids isolated were characterized in the following way: substance A – 3',4',5,7-tetrahydroxyflavone (luteolin); B – 6-C-β-D-glucopyranosyl-3',4',5,7-tetrahydroxyflavone (homoorientin); and C – 7-β-D-glucopyranosyloxy-3',4',5-trihydroxyflavone (cynaroside). This is the first time that luteolin and its C-glycosides have been isolated from *Prunella vulgaris* L.

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FLAVONOIDS OF *Caragana aurantiaca*

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UDC 547.972

The epigeal part of the shrub *Caragana aurantiaca* Koehne. (dwarf pea shrub) collected in the flowering period in the Susamyrskaya valley close to the village of Tunuk (KirghizSSR) has been investigated for the presence of flavonoids.

To obtain the combined flavonoids, 0.9 kg of the dried and comminuted raw material was extracted successively with 40, 70, and 96% ethanol. The ethanolic extracts were evaporated in vacuum to an aqueous residue, which was treated with chloroform to eliminate ballast substances. The flavonoids were extracted from the purified aqueous residue, and the ethyl acetate extract was evaporated in vacuum. The combined flavonoids that precipitated after cooling were separated off by centrifugation, dried, and deposited on a column of polyamide sorbent. Then the flavonoids were eluted successively with water and with various concentrations of ethanol.

Three individual substances were isolated from the dwarf pea shrub and identified.

Substance (I) (eluted with 20% ethanol) was identified as narcissin (isohamnetin 3-O-rutinoside), $C_{28}H_{32}O_{16}$, mp 175-178°C (aqueous ethanol), $[\alpha]_D^{20}$ − 35.7° (s 0.4, ethanol), λ_{max} 360, 257 nm [1, 2].

Substance (II) (eluted with 30% ethanol) was rutin (quercetin 3-O-rutinoside), $C_{27}H_{30}O_{16}$, mp 185-189°C (aqueous ethanol), $[\alpha]_D^{20}$ − 32.4° (s 0.2, methanol), λ_{max} 380, 258 nm [1, 3].

Substance (III) (eluted with 45% ethanol) − $C_{21}H_{20}O_{12}$, mp 258-261°C (aqueous ethanol), λ_{max} 380, 258 nm [1, 3].

Its chromatographic behavior and qualitative reactions showed that substance (III) was a flavonol glycoside.

Acid hydrolysis under mild conditions (0.2% sulfuric acid, 100°C, 30 min) did not split the glycoside into an aglycon and a carbohydrate moiety, which indicated the attachment of the sugar residue in position 7.

Hydrolysis with 5% sulfuric acid gave the aglycon and glucose. The monosaccharide was identified chromatographically. On the basis of its UV spectra and a comparison with authentic samples, the aglycon was identified as quercetin.

All these facts permitted the substance under investigation to be identified as quercimeritrin (quercetin 7-O-glucoside) [1, 3].

This is the first time that substances (I-III) have been isolated from a *Caragana* species.

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