FLAVONOID AGLYCONES OF *Polygonum hydropiper*

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UDC 547.972

Polygonum hydropiper L. (marshpepper smartweed, water-pepper) growing in our country has been studied inadequately from the chemical point of view. Studies on its vitamins are known [1, 2]. G. I. Vysochina [3, 4] investigated the flavonoid aglycones of peppers chemosystematically using paper chromatography and comparison with markers, without the isolation of individual substances and their reliable identification.

In view of the development of drafts of new technical standardization documents for the medicinal raw material "Water-pepper herbage," it was necessary to determine the group of active substances and to develop methods of instrumental analysis for the objective standardization of the raw material. The antihemmorhagic properties that are characteristic for the flavonoid group can be used for standardizing the raw material. This has served as a prerequisite for a more detailed study of the total flavonoids of water-pepper with the isolation of individual substances and their identification.

In the present communication we give the results of a study of the flavonoid aglycones of water-pepper. We used the epigeal parts of plants collected in the flowering phase in the Latvian SSSR in 1981.

To isolate the combined flavonoids, 500 g of dried herbage was treated with chloroform in order to eliminate ballast substances. After the removal of the chloroform, the flavonoids were exhaustively extracted from the raw material with ethyl acetate by repeated extraction with heating on the boiling water bath under reflux. The ethyl acetate extracts were combined, and the solvent was distilled off to dryness. The residue containing the total flavonoids was chromatographed on columns of polyamide sorbent. On elution with 60% ethanol, the combined aglycones, consisting of six components, were obtained.

Rechromatography on a column of polyamide sorbent using mixtures of chloroform and methanol as eluents yielded four free aglycones.

Substance (I) — $C_{15}H_{11}O_7$, mp 310-312°C (from 80% ethanol); $\lambda_{max}^{C_2H_5O}$ 372, 255 nm — was identified as quercetin.

Substance (II) — $C_{15}H_{10}O_6$, mp 276-278°C (60% ethanol); $\lambda_{max}^{C_2H_5OH}$ 368, 253 nm — was kaempferol.

Substance (III) — $C_{16}H_{12}O_7$, mp 303-307°C (from 50% ethanol); $\lambda_{max}^{C_2H_5OH}$ 370, 255 nm — was identified as isorhamnetin [5].

Substance (IV) — $C_{17}H_{13}O_7$, mp 214-217°C (from 96% ethanol); $\lambda_{max}^{C_2H_5OH}$ 373, 255 nm — was determined as rhamnazin [6].

The identification of all the compounds isolated was carried out with the aid of IR and UV spectroscopy, elementary analysis, the results of a study of the products of alkaline degradation, the melting points of the acetyl derivatives, and a chromatographic comparison with authentic samples.

The same aglycones have been detected in samples of water-pepper collected in various regions of the country and obtained from industrial batches of raw material.

LITERATURE CITED

1. N. Ya. Veiderpass and L. A. Kirsh, in: The Public Health Service of Soviet Estonia [in Russian], Tallin, Vol. 3 (1955), p. 201.
2. Proceedings of the Leningrad Institute of Pharmaceutical Chemistry, 12, "Questions of Pharmacognosy" [in Russian], Vol. 1 (1961), p. 179.

Leningrad Institute of Pharmaceutical Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 658-659, September-October, 1984. Original article submitted March 13, 1984.

0009-3130/84/2005-0625$08.50

3. Author's abstract of Candidate's dissertation [in Russian], Tomsk (1969).
4. G. I. Vysochina, in: Plant Resources of Southern Siberia and Methods of Utilizing Them [in Russian], Novosibirsk (1977), p. 55.
5. P. Khozhambergova and K. F. Blinova, Khim. Prir. Soedin., 408 (1979).
6. Be Tkhi Tkhuan' and K. F. Blinova, Rast. Resur., 10, No. 1, 72 (1974).

FLAVONOIDS OF *Glycine hispida*

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UDC 547.972

We have previously reported the isolation of 48 flavonoids and phenolic carboxylic acids from the epigeal part of *Glycine hispida* (Moench) Maxim. (ordinary or hispid soybean) of the Kievskaya variety [1]. Continuing the chemical study of this plant, we have isolated eight glycosides (X-XVII) from ethyl acetate and n-butanolic extracts by chromatography on columns of polyamide and silica gel. The structures of the compounds have been established on the basis of the results of a study of the products of acid, alkaline, and enzymatic hydrolysis, UV, IR, and PMR spectroscopy, and a comparison with authentic samples.

Substance (X) — $C_{21}H_{20}O_9$, mp 233-235°C $[\alpha]_D$ −34.4° (methanol), UV spectrum: λ_{max} 265, 365 nm — was identified as 4',7-dihydroxyisoflavone 7-O-β-D-glucopyranoside (daidzin) [2].

Substance (XI) — $C_{21}H_{20}O_{10}$, mp 253-255°C, $[\alpha]_D$ −25.6° (methanol); UV spectrum: λ_{max} 260, 325 nm. From its IR and PMR spectra it was identical with 4',5,7-trihydroxyisoflavone 7-O-β-D-glucopyranoside (genistin) [2].

Substance (XII) — $C_{22}H_{22}O_9$, mp 210-212°C, $[\alpha]_D$ −26.2° (methanol); UV spectrum, λ_{max} 255 nm. Analysis of the products of the hydrolysis, acetylation, and demethylation of the aglycone, and the absence of a depression of a mixed melting point permitted substance (XII) to be characterized as 7-hydroxy-4'-methoxyisoflavone 7-O-β-D-glucopyranoside (ononin) [2].

Substances (XIII) — $C_{21}H_{20}O_{11}$, mp 178-180°C, $[\alpha]_D$ −16° (methanol) — and (XIV) — $C_{21}H_{20}O_{12}$, mp 218-220°C, $[\alpha]_D$ −39° (methanol) — gave D-glucose and the aglycones kaempferol and quercetin, respectively, on acid hydrolysis. UV spectra with the addition of ionizing reagents, and also PMR spectra showed, in each case, the attachment of the D-glucose residue to the 3-OH group of the aglycone (the anomeric proton gave a doublet in the 5.97-ppm region). Thus, compound (XIII) was kaempferol 3-O-β-D-glucopyranoside (astragalin), and (XIV) was quercetin 3-O-β-D-glucopyranoside (isoquercetrin) [3].

Substance (XV) — $C_{27}H_{30}O_{16}$, mp 188-190°C, $[\alpha]_D$ −29° (DMFA) — was identified on the basis of chemical transformations and the products of acid and enzymatic hydrolysis, spectral characteristics, and the results of a comparison with an authentic sample as quercetin 3-O-rutinoside (rutin) [3].

Substance (XVI) — $C_{27}H_{30}O_{15}$, mp 220-222°C. UV spectrum: λ_{max} 365, 347 nm. Kaempferol, D-glucose, and L-rhamnose were detected in the products of alkaline hydrolysis. Kaempferol and rutinose were found among the products of enzymatic hydrolysis. On the basis of the facts given above and PMR-spectral characteristics, compound (XVI) was identified as kaempferol 3-O-rutinoside [4].

Substance (XVII) — $C_{27}H_{30}O_{17}$, mp 198-200°C. UV spectrum: λ_{max} 265, 355 nm. Quantitative acid hydrolysis showed the presence in the molecule of two glucose residues and of the aglycone quercetin. The oxidation of (XVII) by Chandler's method [4] followed by the paper chromatography of the biose split out and visualization with specific reagents permitted the assumption of the existence of a 1→2 bond between the D-glucose residues. On the basis of the facts given, substance (XVII) was characterized as quercetin 3-O-sophoroside [3].

Khar'kov Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 659-660, September-October, 1984. Original article submitted April 10, 1984.

 0009-3130/84/2005-0626$08.50