FLAVONOIDS OF Polygonum lapathifolium

T. G. Kul'pina, G. I. Vysochina, and T. P. Berisovskaya

UDC 582.657/581.192

According to previous reports [1-3], the epigeal part of Polygonum lapathifolium L. contained flavonoid glycosides: avicularin, hyperin, quercimeritrin, rutin, quercetin, 3-O-β-D-glucoside 2"-gallate, quercitrin, isoquercitrin, quercetin 3-glucoside, and kaempferol 3-glucoside 2'-gallate.

There is no information on the flavonoid glycosides of Siberian polygonums.

We have studied the flavonoid compounds of the epigeal part and leaves of Polygonum lapathifolium L. (curltop lady's thumb) collected in various regions of Siberia.

To isolate the flavonoids, the air-dry raw material was exhaustively extracted with 96% and 80% ethanol in the boiling water bath. The extracts were investigated by two-dimensional chromatography on FN-15 paper (direction I: propanol–formic acid–water (2:5:5); direction II: butan-1-ol–glacial acetic acid–water (40:12:28). Both in the leaves and in the epigeal part, 16 substances of flavonoid nature were determined, namely: two free aglycones – quercetin and kaemferol – and 14 glycosides, of which six were identified. The remaining glycosides were present in insignificant amounts.

To determine the bound aglycons, the extract was hydrolyzed with 5% sulfuric acid, and the combined aglycons were extracted with diethyl ether and separated on a column of L 40/100 silica gel (with ethyl formate–formic acid–toluene (4:1:5) as eluent).

Two aglycons were isolated which were identified on the basis of PC, TLC in various solvent systems in comparison with authentic samples, and also by spectral analysis [4-6] as kaempferol and quercetin.

The glycosides were identified on the basis of the results of an investigation by spectral analysis of the eluates (60% ethanol, dynamic elution) after two-dimensional paper chromatography and by determinations after recrystallization, of melting points and specific rotations. By means of UV spectroscopy using diagnostic additives it was established that in all the aglycons the sugar component was attached in the C-3 position. The aglycons and the sugars were determined after hydrolysis with 5% hydrochloric acid [5] using TLC on Silufol plates in various solvent systems in parallel with marker substances. On hydrolysis, glycoside 1 gave quercetin and glucose; 2 gave quercetin and galactose; 3 gave quercetin, glucose, and gallic acid, 4 gave quercetin and arabinose; 5 gave kaempferol and galactose; and 6 gave kaempferol, glucose, and gallic acid.

Thus, from the results of spectral analysis, melting points, and specific rotations the following substances were identified.

1. Quercetin 3-O-β-D-glucopyranoside, $C_{21}H_{20}O_{12}$, mp 223-225°C $[\alpha]_D^{20}$ −15° (c 1.0; methanol);

2. Quercetin 3-O-β-D-galactopyranoside, $C_{21}H_{20}O_{12}$, mp 236-238°, $[\alpha]_D^{20}$ −125° (c 1.0; methanol);

3. Quercetin 3-O-β-D-glucopyranoside 2"-gallate, $C_{28}H_{24}O_{16}$, mp 205°, $[\alpha]_D^{20}$ −70° (c 1.0; methanol);

4. Quercetin 3-O-α-D-arabofuranoside, $C_{20}H_{18}O_{11}$, mp 217-218°;

5. Kaempferol 3-O-β-D-gallactopyranoside, $C_{21}H_{20}O_{11}$, mp 228-230°, $[\alpha]_D^{20}$ −45° (c 1.0; methanol);

Central Siberian Botanical Garden, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Tomsk Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 511-512, July-August, 1986. Original article submitted January 28, 1986.

0009-3130/86/2204-0481$12.50 © 1987 Plenum Publishing Corporation

6. Kaempferol 3-O-β-D-glucoside 2"-gallate, $C_{28}H_{24}O_{15}$, mp 227-229°, $[\alpha]_D^{20}$ −84° (c 1.0; methanol).

LITERATURE CITED

1. Kh. Kh. Khalmatov, Plants of Uzbekistan with a Diuretic Action [in Russian], Tashkent (1979), p. 180.
2. T. Isobe, N. Ito, and Y. Noda, Phytochemistry, 19, No. 8, 1877 (1980).
3. T. Isobe, T. Fukushige, and Y. Noda, Chem. Lett., No. 1, 27-30 (1979).
4. L. K. Klyshev, V. A. Bandyukova, and L. S. Alyukina, Plant Flavonoids [in Russian], Alma-Ata (1978), p. 220.
5. T. J. Mabry, K. R. Markham, and M. V. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970), p. 353.
6. T. A. Geissman, The Chemistry of Flavonoid Compounds, Pergamon, Oxford (1962), pp. 107-155.

FLAVONOIDS, PHENOLIC ACIDS, AND HYDROXYCOUMARINS FROM THE FRUIT OF VARIOUS SPECIES OF THE GENUS Berberis

V. V. Vereskovskii and D. K. Shapiro

UDC 581.6:582.677.3:581.19

Continuing a study of the fruits of five species of barberry (Family Berberidaceae) [1, 2], we have investigated the phenolic compounds.

The dry comminuted fruits of Berberis vulgaris L., B. coreana Palib., B. sieboldii Miq., B. integerrima Bunge, and B. sphaerocarpa Kar. et Kir. (20-50 g of each species), freed from seeds, were extracted with 80% ethanol three times in the water bath at the boiling point of the solvent in a flask with a reflux condenser. In each case, the combined extract was filtered, evaporated to an aqueous residue, and mixed with Woelm DC polyamide (FRG). After this, the mixture obtained was dried at 60°C, ground, and filled into a column. The substances were eluted with distilled water and with 10, 50, and 96% ethanol. The fractions collected were chromatographed by the two-dimensional ascending method on Filtrak FN 12 paper in two solvent systems: 1) butan-1-ol–CH_3COOH (glacial)–H_2O (3:1:1) and 2) 15% acetic acid (second direction). Some of the fractions were combined and evaporated to dryness, and the residues were dissolved in 50 ml of 80% ethanol. These solutions were used for hydrolysis and the subsequent identification of the phenolic compounds.

The hydrolysis of ethanolic extracts of the fruits of five species of barberry showed that the flavonoid glycosides were represented by five aglycones – quercetin, isorhamnetin, kaempferol, apigenin, and luteolin, which we identified chromatographically with authentic samples and by spectral analysis [3, 4].

The separation of the phenolic substances was carried out in the same solvents by paper chromatography. It was established that the fruits of these species of barberry contained 15 compounds of flavonoid nature and one compound of hydroxycoumarin nature, together with four phenolic acids [3, 5].

The individual components of the phenolic substances and the hydroxycoumarin compound were obtained by preparative paper chromatography of the ethanolic extracts in the systems given above. The spots of the substances were eluted from the chromatograms with 96% ethanol. From the result of the Bryant cyanidin reaction, substances 1-11 were assigned to the glycosides and 12-15 to the flavonoid aglycons. These substances were identified by acid hydrolysis, paper chromatography with markers, and specific color reactions, and also by a study of their spectral characteristics in the UV region with diagnostic reagents [6].

The phenolic carboxylic acids and the hydroxycoumarin compounds were studied from their fluorescence in UV light (λ 254 and 360 nm) in the presence of ammonia and in its absence,

Central Botanical Garden, Academy of Sciences of the Belorussian SSR, Minsk.

Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 512-513, July-August, 1986. Original article submitted February 6, 1986.

0009-3130/86/2204-0482$12.50

© 1987 Plenum Publishing Corporation