FLAVONOIDS OF *Hypericum aucherii*

G. M. Kitanov, K. F. Blinova,
Kh. Akhtardzhiev, and V. Rumenin

UDC 547.972

Continuing a study of Bulgarian representatives of the genus *Hypericum* L., we have investigated the epigeal parts of *H. aucherii* Jaub. et Spach. [1]. By two-dimensional chromatography on paper, in an ethanolic extract of the herb we detected the presence of more than 20 phenolic compounds belonging to the classes of phenolic carboxylic acids, flavonoids, and xanthones. In the present paper we give the results of a study of some of the flavonoid compounds.

The raw material (1.5 kg, air-dry weight) was exhaustively extracted with 80% ethanol. The extract was concentrated until the ethanol had been eliminated, hot water was added, and the precipitate that deposited was filtered off. The filtrate was purified with chloroform and the total phenolic compounds were extracted with ethyl acetate. Five individual substances were isolated from the ethyl acetate by column chromatography on polyamide and by preparative paper chromatography. Substance (I) was present in the extract in only very small amounts and it was impossible to isolate it in the crystalline form. By qualitative reactions, UV spectroscopy, and chromatography with an authentic sample it was identified as kaempferol [2].

Substance (II) (178 mg) had mp 311-312°C. A comparison of physicochemical constants and spectral characteristics (UV, IR, and PMR spectra) enabled (II) to be identified as quercetin.

Substance (III) (150 mg) had mp 325-330°C (decomp.), λ_{max}^{MeOH} 254, 376 nm. In the presence of sodium methanolate and sodium acetate the substance rapidly decomposed, which shows the vicinal position of the hydroxy groups in the molecule. This was confirmed by the reaction with ferric chloride (blue-brown coloration) and with alkaline solutions (green coloration). The PMR spectrum (δ scale, ppm) — 6.40 (d, J = 2 Hz, 1 H, H-8), 6.20 (d, J = 2 Hz, 1 H, H-6), and 7.30 (s, 2 H, H-2', H-6') — showed that the vicinal hydroxy groups were present in positions 3',4', and 5' of ring B. Thus, substance (III) was identified as 3,3',4',5,5',7-hexahydroflavone (myricetin).

Two-dimensional chromatography showed that substance (IV) was a mixture of three flavonoid glycosides. It was impossible to separate them by fractional crystallization. The separation of 1 g of the mixture of glycosides was achieved in a column of cellulose sorbent with elution by ethyl acetate—acetone—water (50:1:5). After recrystallization from 20% ethanol, yellow crystals were obtained with mp 220-222°C, λ_{max}^{MeOH} (nm, log ε) 258, 360 (4.22, 4.08), R_f 0.35 (15% AcOH) and 0.60 [BAW (40:10:22)]. The $E_{1\,cm}^{1\%}$ value characterized it as a monoside. On acid hydrolysis with 5% HCl, substance (IV) rapidly split into quercetin and glucose. Spectral investigations in the UV region showed that the glucose was bound to the aglycone in position 3. The features of its IR spectrum (1080, 1020, 1001, and 895 cm^{-1}) showed the pyranose form of the sugar and the β-configuration of the glycosidic bond. Consequently, substance (IV) was quercetin 3-O-β-D-glucoside (isoquercitrin). This was confirmed by a chromatographic comparison with an authentic sample of isoquercitrin. This glycoside has been isolated only from *H. inodorum* Willd. among species of the genus *Hypericum* [3].

Substance (V) (356 mg) with mp 242-244°C has been provisionally assigned to the flavone aglycones on the basis of its chromatographic behavior, reactions with diagnostic reagents, and UV spectra.

Leningrad Institute of Pharmaceutical Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 854-855, November-December, 1979. Original article submitted July 17, 1979.

 0009-3130/79/1506-0760$07.50

LITERATURE CITED

1. G. Kitanov and K. F. Blinova, Khim. Prir. Soedin., 524 (1978).
2. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
3. G. G. Zapesochnaya, L. G. Kuptsova, T. V. Kashtymova, A. I. Ban'kovskii, and T. A. Mel'nikova, Khim. Prir. Soedin., 279 (1967).

FLAVONOIDS OF SOME SPECIES OF *Euphorbia*

V. A. Soboleva

UDC 547.972:582.757

We have previously reported the isolation from the herb *Euphorbia kaleniczenkii* of five substances of flavonoid nature, while quercetin and hyperoside proved to be common to the 15 species of *Euphorbia* investigated in parallel [1]. Continuing the chemical study of *Euphorbia seguieriana* Neck., *E. virgultosa* Klok., and *E. semivillosa* Prokh., we have isolated and identified from *E. seguieriana* the aglycone myricetin and its glycoside isomyricitrin, while kaempferol and gallic, caffeic, chlorogenic, and neochlorogenic acids proved to be common to the three above-mentioned *Euphorbia* species [2].

For further separation of the total polyphenolic complexes of these plants, concentrated ethanolic extracts were treated with various organic solvents, after which we used chromatography on polyamide with elution by water at various temperatures. As a result of the investigation, three flavonoid compounds, one hydroxybenzoic acid derivative, one coumarin, and gypsogenic acid have been isolated.

The substances were identified on the basis of chromatographic analysis, melting points, chemical transformations (alkaline cleavage, acid and enzymatic hydrolyses), IR and UV spectroscopy with ionizing and complex-forming reagents [3, 4], and comparison with authentic samples.

Substance (I), $C_{21}H_{20}O_{11}$, mp 174-176°C, isolated from *E. virgultosa* was identified as kaempferol 3-O-β-D-glucopyranoside (astragalin).

Substance (II), $C_{21}H_{20}O_{12}$, mp 229-231°C, isolated from *E. seguieriana* and *E. semivillosa* was identified as quercetin 3-O-β-D-glucopyranoside (isoquercitrin) [5].

Substance (III), $C_{27}H_{30}O_{16}$, mp 188-190°C, isolated from *E. seguieriana* and *E. semivillosa*, giving no intermediate monoglycoside on stepwise hydrolysis under the usual conditions, was characterized as rutin [6].

Substance (IV), $C_8H_8O_5$, mp 156-157°C, isolated from the three species of *Euphorbia* investigated was identified as methyl gallate.

Substance (V), $C_{10}H_8O_4$, with mp 203-205°C, consisted of 7-hydroxy-6-methoxycoumarin (scopoletin), and substance (VI) can be assigned, on the basis of qualitative reactions and transformation products, to the triterpene glycosides forming derivatives of gypsogenic acid.

This is the first time that substances (V) and (VI) have been detected in and isolated from *E. seguieriana*.

LITERATURE CITED

1. V. A. Soboleva and R. K. Chagovets, Khim. Prir. Soedin., 528 (1971).
2. O. M. Bondarenko, V. A. Soboleva, and R. K. Chagovets, in: Pharmacy [in Russian], Kiev, No. 2 (1975), p. 36.
3. I. P. Kovalev and V. I. Litvinenko, Khim. Prir. Soedin., 233 (1965).
4. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
5. O. M. Bondarenko and V. I. Litvinenko, Khim. Prir. Soedin., 597 (1969).
6. V. I. Litvinenko and T. P. Nadezhdina, Rast. Res., 4, 68 (1968).

Khar'kov Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 855-856, November-December, 1979. Original article submitted July 24, 1979.

0009-3130/79/1506-0761$07.50