# BIFLAVONE, FLAVONOL, AND XANTHONE GLYCOSIDES FROM Hypericum aucheri

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UDC 547.972

From the epigeal part of Hypericum aucheri Jaub. et Spach we have previously isolated kaempferol, quercetin, myricetin, isoquercitrin, and flavonoid (V) [1] and also 1,3,6,7-tetrahydroxyxanthone and its 2-C-glucosid (mangiferin) [2, 3]. On the basis of its UV, IR, PMR, and mass spectra, substance (V) was provisionally identified as 3,8"-bisapigenin [4]. In the present communication we give additional information on the identification of the flavonoid (V) and present results on the isolation and study of glycosides.

The $^{13}$C NMR spectrum of substance (V) (20.15 MHz; DMSO-$d_6$; ppm) contained the following signals: 163.5 (C-2); 110.3 (C-3); 180.4 (C-4); 162.2 (C-5); 98.9 (C-6); 164.3 (C-7); 93.7 (C-8); 157.4 (C-9); 99.4 (C-10); 123.1 (C-1'); 127.8 (C-2', C-6'); 115.2 (C-3', C-5'); 161 (C-4'); 163.6 (C-2"); 102.8 (C-3"); 181.7 (C-4"); 159.7 (C-5"); 98.7 (C-6"); 161.6 (C-7"); 103.1 (C-8"); 154.9 (C-9"); 103,8 (C-10"); 121.3 (C-1"); 129.4 (C-2"', C-6"'), 115.9 (C-3"', C-5"'); 161.0 (C-4"'). The chemical shifts of the signals in the $^{13}$C spectrum were assigned to the corresponding carbon atoms by comparison with literature information. The presence of a $C_3-C_{8''}$ carbon bond in the structure of the bisapigenin was confirmed by signals at 110.3 ppm (C-3) and 103.1 ppm (C-8"), while the corresponding signals in the apigenin molecule have values of 102.8 ppm (C-3) and 94.0 ppm (C-8) [5]. This is the first time that 3,8"-bisapigenin has been isolated from a natural source and it is the first biflavone found in species of the genus Hypericum. The isolation of a biflavone from representatives of the genus Hypericum L. confirms the reality of the existence of the subfamily Hypericoidea Engl. as part of the family Guttiferae Juss. [4, 6].

The mangiferin isolated previously (9.75 g) was the main component of the mixture of polyphenols [2]. It was identified with the aid of UV, IR, PMR and mass spectra [7], and also by decomposition with HI in phenol.

Glycosides were extracted and partially separated as described in the literature [1, 4]. Repeated preparative paper chromatography and purification on columns of polyamide gave eight substances (VIII—XV).

Substance (VIII) (4 mg), with mp 260-263°C and $\lambda_{\max}^{\mathrm{MeOH}}$ 242, 258, 320, and 370 was a xanthone C-glycoside [3]. It did not change under the conditions of acid hydrolysis. By comparing the characteristics found with literature information and by a chromatographic comparison with an authentic sample, it was identified as 4-C-glucosyl-1,3,6,7-tetrahydroxyxanthone (isomangiferin).

Substances (IX—XV) were monoglycosides of Kaempferol, quercetin, and Myricetin.

Substance (IX) (7 mg) was astragalin (kaempferol 3-glucoside), mp 179-181°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 266, 352 nm.

Substance (X) (12 mg) was hyperoside (quercetin 3-galactoside), mp 235-237°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 258, 358 nm.
Substance (XI) (73 mg) was quercitrin (quercetin 3-rhamnoside), mp 175-177°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 260, 360 nm.

Substance (XII) (92 mg) was miquelianin (quercetin 3-glucuronide), mp 182-184°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 257, 362 nm.

Substance (XIII) (7 mg) was myricetin 3-glucoside, mp 222-226°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 257, 365 nm.

Substance (XIV) (4 mg) was myricitrin (myricetin 3-rhamnoside), mp 185-187°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 260,366 nm.

Substance (XV) (5 mg) was myricetin 3-glucuronide, mp 180-182°C, $\lambda_{\max}^{\mathrm{MeOH}}$ 264, 372 nm.

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Scientific Institute of Pharmacology and Pharmacy of the Medical Academy, Sofia. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 454-455, May-June, 1988. Original article submitted November 30, 1987.

All the compounds were identified from the results of chromatographic analysis, UV spectroscopy, and acid hydrolysis. Spectral investigations in the UV region showed that in each of the glycosides the sugar was attached to the aglycone in the third position. The glycosides were hydrolyzed with 1% HCl for 10-20 min, and the uronides with 5% $H_2SO_4$ for 60-90 min. Substances (IX), (X), (XI), (XII), and (XIV) were also compared with authentic samples.

Substance (XVI) (3.2 g) was chlorogenic acid, mp 202-204°C, $\lambda_{max}^{MeOH}$ 240 sh., 303 sh., 329 nm. It was identified with the aid of the usual spectroscopic and chromatographic methods and by comparison with an authentic sample.

This is the first time that substances (IX), (XIII), and (XV) have been detected in and isolated from a representative of the genus *Hypericum*. Substance (XII) (miquelianin) has recently been isolated from H. *hirsutum* L., and (XIV) (myricitrin) from *H. rochelii* Griseb. et Schenk and from *H. boissieri* Petr. Isomangiferin has also been found in trace amounts in plants of the same species [8, 9].

## LITERATURE CITED

1. G. Kitanov, K. F. Blinova, K. F. Akhtardzhiev, and V. Rumenin, Khim. Prir. Soedin., 854 (1979).
2. G. Kitanov and K. F. Blinova, Khim. Prir. Soedin., 524 (1978).
3. G. Kitanov and K. F. Blinova, Khim. Prir. Soedin., 256 (1980).
4. G. Kitanov, Farmatsiya (Sofia), No. 5, 13 (1985).
5. K. R. Markham and V. M. Chari, in: The Flavonoids: Advances in Research (ed. J. B. Harbone and T. J. Mabry), Chapman and Hall, London (1982), p. 19.,
6. G. Kitanov and K. F. Blinova, Khim. Prir. Soedin., 185 (1987).
7. O. A. Denisov, V. I. Glyzin, S. V. Rusakova, and M. G. Pimenov, Khim. Prir. Soedin., 283 (1977).
8. G. Kitanov, Khim. Prir. Soedin., 132 (1988).
9. G. Kitanov, Papers at the Fourth National Conference. Botany [in Bulgarian], Sofia, Vol. 1, 91 (1987).