FLAVONOIDS OF *Hedysarum setigerum*

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Plants of the *Hedysarum* (Fabaceae) genus are distributed in Eurasia. Several species have been successfully used in folk medicine [1]. The wide range of therapeutic action for *Hedysarum* is due to the presence of immunomodulating, antiviral, and anti-inflammatory agents.

We investigated *H. setigerum* Turcz. ex Fischer et Meyer [3], which is endemic to Siberia and has not been previously studied.

The epigeal part of the plant that was collected during flowering on the west shore of Lake Baikal was extracted with MeOH (80%). The evaporated extract was successively extracted with CH_2Cl_2 and *n*-BuOH. The butanol extract was dissolved in MeOH and precipitated with acetone (1:1 by vol). The precipitate was separated. The supernatant was chromatographed over polyamide (sorbent:compound, 10:1) using H_2O—MeOH to give fractions containing five flavonoids. Column chromatography over SiO_2, flash chromatography (SiO_2, polyamide), and preparative TLC on polyamide isolated pure **1**-**3**. Compounds **4** and **5** could not be separated under these conditions. The compounds were identified by spectral methods (including 2D NMR) using combined **4** and **5** in a 4:3 ratio.

Isorhamnetin (1): $C_{16}H_{12}O_7$, mp 290-292°C (MeOH) [4], M.W. (MALDI), *m*/*z*: 317.5 $[M + H]^+$.

Avicularin (2): $C_{20}H_{20}O_{11}$, mp 208-209°C (MeOH), $[\alpha]_{546}^{20}$ -191.8° (*c* 0.50, MeOH) [5], M.W. (MALDI), *m*/*z*: 435.6 $[M + H]^+$, 457.6 $[M + Na]^+$.

Rhoifolin (3): $C_{27}H_{30}O_{14}$, mp 200-202°C (MeOH), $[\alpha]_{546}^{20}$ -119.6° (*c* 0.56, MeOH) [6], M.W. (MALDI), *m*/*z*: 579.7 $[M + H]^+$, 601.7 $[M + Na]^+$.

Physicochemical constants and spectral properties of **1**-**3** correspond with those reported [4-6].

Linarin (4) $C_{28}H_{32}O_{14}$ and **diosmin (5)** $C_{28}H_{32}O_{14}$, M.W. (MALDI), *m*/*z*: 593.6 $[M + H]^+$, 615.6 $[M + Na]^+$ and 609.5 $[M + H]^+$, 631.6 $[M + Na]^+$, respectively.

NMR and mass spectra indicate that **4** and **5** are biosides and differ in the substitution on ring B. ^1H and ^{13}C NMR indicate that the carbohydrate fragments in **4** and **5** are identical and correspond to rutinosides [7-10]. Protons of diosmin B-ring in the ^1H NMR spectrum give three signals; of linarin, two signals with doubled intensity.

Table 1 lists ^1H and ^{13}C spectral data for the aglycones of **4** and **5**.

Compounds **1** and **3**-**5** are observed for the first time in the *Hedysarum* genus.

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TABLE 1. ^{1}H and ^{13}C NMR Spectra of **4** and **5** (400 MHz, δ, ppm, J/Hz, DMSO-d_6)

Atom	**4**		**5**	
	^{13}C	^{1}H	^{13}C	^{1}H
2	164.52		164.72	
3	95.33	6.80 (s)	95.33	6.70 (s)
4	182.46		182.54	
5	161.65		161.65	
6	101.02	6.47 (d, 2.2)	101.02	6.48 (d, 2.2)
7	162.96		163.45	
8	105.96	6.79 (d, 2.2)	104.31	6.76 (d, 2.2)
9	157.46		157.50	
10	105.98		105.96	
1′	123.18		123.45	
2′	128.99	8.10 (dd, 8.8, 2.2)	113.60	7.40 (d, 2.3)
3′	115.24	7.15 (dd, 8.8, 1.7)	147.28	
4′	161.69		151.85	
5′	115.24	7.15 (dd, 8.8, 1.7)	112.78	7.11 (d, 8.6)
6′	128.99	8.10 (dd, 8.8, 2.2)	119.47	7.50 (dd, 8.6, 2.3)
-OH (5)		12.90 (s)		12.90 (s)
$-OCH_3$	56.30	3.88 (s)	56.08	3.90 (s)

REFERENCES

1. V. V. Telyat′ev, *Useful Plants of Central Siberia* [in Russian], Vost.-Sib. Knizh. Izd., Irkutsk (1987).
2. *Plant Resources of the USSR. Flowering Plants, Their Chemical Composition and Use. Hydrangeaceae-Haloragaceae Families* [in Russian], Nauka, Leningrad (1987).
3. V. L. Komarov, ed., *Flora of the USSR*, Izd. Akad. Nauk SSSR, Moscow (1948), Vol. 13.
4. V. K. Kurkin, V. B. Braslavskii, G. G. Zapesochnaya, and V. O. Tolkachev, *Khim. Prir. Soedin.*, 548 (1990).
5. V. N. Spiridonov, *Dokl. Akad. Nauk SSSR*, **169**, 1, 126 (1966).
6. H. Wagner, G. Aurnhammer, L. Horhammer, and L. Farkas, *Chem. Ber.*, **102**, 2083 (1969).
7. L.-J. Chen and G. Hrazdina, *Phytochemistry*, **20**, 297 (1981).
8. J. C. Park, J. H. Lee, and J. S. Choi, *Phytochemistry*, **39**, 261 (1995).
9. N. N. Trofimova, A. S. Gromova, V. I. Lutskii, A. L. Vereshchagin, and A. A. Semenov, *Khim. Prir. Soedin.*, 723 (1992).
10. Y. C. Kim, R. Higuchi, Y. Kitamura, and T. Komori, *Liebigs Ann. Chem.*, 1285 (1991).