

## FLAVONOIDS OF THE EPIGEAL PART OF *Onobrychis arenaria*

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Plants of the genus *Onobrychis* Mill. (fam. Fabaceae) are a rich source of flavonoids, and some of them are used in folk medicine for metrorrhagias and as potency-enhancing agents. Preparations of individual flavonoids and of the total mixture possess a hypolipidemic activity [1].

In the present communication we give the results of a study of the flavonoids of the epigeal part of Hungarian sainfoin *O. arenaria* (Kit.) DC, gathered in July, 1991 in the environs of Lake Issyk-Kul' [2]. An alcoholic extract of the ground air-dry raw material was concentrated in vacuum, diluted with water, and re-extracted successively with chloroform, ethyl acetate, and *n*-butanol. Chromatography of the ethyl acetate fraction on a column of silica gel in a gradient chloroform-methanol system led to the isolation of compounds (1)-(3).

For the identification of the substances isolated we used UV, PMR, and mass spectra and the results of chemical transformations.

**Nicotiflorin (1)**, (kaempferol 3-O-rutinoside) — yellow crystals with the composition  $C_{27}H_{30}O_{15}$ , mp 215-217°C,  $\lambda_{\max}$  265, 352 nm. The acetylation of substance (1) with acetic anhydride in pyridine gave the nonaacetyl derivative with mp 142-144°C ( $M^+$  972).

The acid hydrolysis of flavonoid (1) formed kaempferol (3,4',5,7-tetrahydroxyflavone), *D*-glucose, and *L*-rhamnose. The presence of terminal *L*-rhamnose in the (1) molecule was confirmed by the formation of kaempferol 3-O- $\beta$ -*D*-glucoside (astragaline) with mp 178-179°C by the partial hydrolysis of glycoside (1).

**Narcissin (2)** (isorhamnetin 3-O-rutinoside) — yellow crystals with the composition  $C_{28}H_{32}O_{16}$ , mp 178-180°C,  $\lambda_{\max}$  (ethanol) 254, 265, 356 nm. In the PMR spectrum of compound (2), in addition to the signals of the protons of the aglycon, signals appeared of the anomeric protons of *L*-rhamnose (5.19 ppm, br.s) and of *D*-glucose (5.45 ppm, d, 6.5 Hz), of the  $CH_3$  group of rhamnose (1.45 ppm, br.s) and of other protons of the carbohydrate moiety in the 3.75-4.52 ppm interval. The acid hydrolysis of glycoside (2) gave isorhamnetin ( $C_{16}H_{12}O_7$ , mp 305-307°C,  $M^+$  316,  $\lambda_{\max}$  255, 266, 372 nm), *D*-glucose, and *L*-rhamnose.

The acetylation of glycoside (2) with acetic anhydride in pyridine gave the nonaacetyl derivative with the composition  $C_{46}H_{50}O_{25}$ , mp 117-119°C, the mass spectrum of which contained, in addition to the peak of the molecular ion with  $m/z$  1002, intense peaks of fragmentary ions: of an acylated biose with  $m/z$  561 and of terminal rhamnose with  $m/z$  273, 213, and 153 [4].

The partial hydrolysis of glycoside (2) with 10% acetic acid led to isorhamnetin 3-O- $\beta$ -*D*-glucopyranoside with the composition  $C_{22}H_{22}O_{12}$ , mp 163-165°C,  $\lambda_{\max}$  257, 267, 360 nm [5].

**Arbutin (3)** (hydroquinone O- $\beta$ -*D*-glucoside) —  $C_{12}H_{16}O_7$ , mp 159-161°C,  $\lambda_{\max}$  (ethanol) 285 nm. The acid hydrolysis of substance (3) gave hydroquinone and *D*-glucose [6].

This is the first time that compounds (1)-(3) have been isolated from *O. arenaria*.

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