

## FLAVONOIDS OF *Psoralea drupaceae* AND *Reseda luteola*

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Plants of the genus *Psoralea* L. (fam. Fabaceae) are rich in furocoumarins, and some of them exhibit an antiasthmatic, antihysterical, and antiepileptic action. The drugs psoralen and psoboran are used in officinal medicine as photosensitizing agents for treating vitiligo and alopecia areata [1].

The furocoumarins psoralen and angelicin have been detected previously in the roots of *Psoralea drupaceae* Bunge (drupe scurf pea) [2, 3].

The comminuted air-dry roots of the plant (400 g) gathered in September, 1989, in the environs of Alimtau, Republic of Kazakhstan, were exhaustively extracted with ethanol. The alcoholic extract was concentrated in vacuum, diluted with water, and extracted successively with chloroform and ethyl acetate. Chromatography of the chloroform fraction on silica gel in the hexane-chloroform (9:1) system led to the isolation of psoralen and angelicin.

Chromatography of the ethyl acetate fraction on silica gel in the chloroform-methanol (9:1) system led to the isolation of flavonoid (1).

**Daidzin (1)** (daidzein 7-O- $\beta$ -D-glucopyranoside) — C<sub>21</sub>H<sub>20</sub>O<sub>9</sub>, mp 235-236°C,  $\lambda_{\max}$  263, 315 nm. The UV spectrum was characteristic for isoflavone derivatives.

The PMR spectrum showed signals of the protons H-5 (8.18 ppm, d, 8.0 Hz), H-2 (7.93 ppm, s), H-6 (7.18 ppm, dd, 8.0 and 2.0 Hz), and H-8 (7.04 ppm, d, 2.0 Hz), of an anomeric proton (5.63 ppm, d, 6.5 Hz), and of the other protons of the carbohydrate moiety (3.90-4.55 ppm).

The acid hydrolysis of substance (1) gave daidzein (4',7-dihydroxyisoflavone, C<sub>15</sub>H<sub>10</sub>O<sub>4</sub>, mp 276-277°C, M<sup>+</sup> 254) and D-glucose. The acetylation of glycoside (1) gave a pentaacetate with mp 185-187°C the PMR spectrum of which contained the signals of four acetoxy groups, a glucose residue, and one ArOCOCH<sub>3</sub> group [4].

This is the first time that daidzin has been isolated from *P. drupaceae*.

Plants of the *Reseda* L. genus (fam. Resedaceae) form a rich source of flavonoids. The epigeal parts of the plants are used as diuretic and sudorific agents. The flowers have long been used for dyeing silk yellow. Some flavonoids of the plants increase the resistance of capillaries and exert a cholagogic action [5]. Luteolin, cynaroside, luteolin 3'-O- $\beta$ -D-glucofuranoside, apigenin, and luteolin 3',7-diglucoside have previously been isolated from this plant [5, 7].

The epigeal part of *R. luteola* L. (weld mignonette) was gathered in the flowering period in 1984 in the environs of Tashkumir, Republic of Kyrgyzstan. An alcoholic extract from the comminuted air-dry raw material was concentrated in vacuum, diluted with water, and extracted successively with chloroform and ethyl acetate. Chromatography of the ethyl acetate fraction on a column of silica gel in a gradient system of chloroform and propan-2-ol led to the isolation of luteolin, cynaroside, and flavonoids (2) and (3).

**Kaempferol 3-O- $\beta$ -D-glucoside 7- $\alpha$ -L-rhamnoside (2)** — C<sub>27</sub>H<sub>30</sub>O<sub>15</sub>, mp 190-192°C,  $\lambda_{\max}$  258, 266, 352 nm, which are characteristic for 3-O-substituted flavonols.

The PMR spectrum (in Py-d<sub>5</sub>) showed signals of the protons of the CH<sub>3</sub> group of rhamnose at 1.52 ppm (d, 6.5 Hz), of the anomeric protons of L-rhamnose at 5.21 ppm (br.s) and of D-glucose at 5.52 ppm (d, 6.5 Hz), of the protons of the sugar moiety at 3.74-4.68 ppm, and of the protons of aromatic rings at 6.64 ppm (d, 2.0 Hz, H-6), 6.80 ppm (d, 2.0 Hz, H-8), 7.14 ppm (d, 8.5 Hz, H-3',5'), and 8.30 ppm (m, H-2',6').

Acid hydrolysis gave kaempferol (3,4',5,7-tetrahydroxyflavone — C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>, M<sup>+</sup> 286, mp 275-277°C), D-glucose, and L-rhamnose.

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The acetylation of substance (2) with acetic anhydride in pyridine gave a nonacetate derivative with the composition  $C_{45}H_{48}O_{24}$  the mass spectrum of which showed, in addition to the peak of the molecular ion with  $m/z$  972, intense peaks of fragment ions: of an acylated tetraacetylhexose with  $m/z$  331, 271, and 169, and of a triacetylramnose with  $m/z$  273, 213, and 153 [7].

**Brassidin (3)** (isorhamnetin 3-O- $\beta$ -D-glucoside 7- $\alpha$ -L-rhamnoside) –  $C_{28}H_{32}O_{16}$ , mp 219-221°C,  $\lambda_{max}$  255, 266, 356 nm, which are characteristic for 3-substituted flavonols.

In the PMR spectrum (in Py- $d_5$ ) of compound (3), in addition to the signals of the protons of the aglycon, we observed signals of the anomeric protons of L-rhamnose (5.18 ppm, br.s), and of D-glucose (5.47 ppm, d, 6.5 Hz), of the  $CH_3$  group of rhamnose (1.47 ppm, br.s), and of the other protons of the carbohydrate moiety in the 3.76-4.65 ppm interval. On acid hydrolysis, glycoside (3) gave isorhamnetin ( $C_{16}H_{12}O_7$ , mp 305-307°C,  $M^+$  316,  $\lambda_{max}$  255, 266, 370 nm), D-glucose, and L-rhamnose.

The acetylation of glycoside (3) with acetic anhydride in pyridine gave a nonacetyl derivative with the composition  $C_{45}H_{50}O_{25}$ , mp 116-118°C, the mass spectrum of which contained, in addition to the peak of the molecular ion with  $m/z$  1002, intense peaks of fragment ions: of an acylated tetracetylglucose with  $m/z$  331, 271, 169, and of triacetylramnose with  $m/z$  273, 213, 153 [8].

This is the first time that compounds (2) and (3) have been isolated from *R. luteola*.

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