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Abstract

Full Text

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Galein—a New Flavonoid from Goat' s Rue, *Galega officinalis* L.

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Goat' s rue, *Galega officinalis* L., is a perennial herbaceous plant of the legume family.

Goat's rue is of interest for investigation as a valuable medicinal and fodder plant ([1–3]). Chemical investigation of the seeds of goat' s rue showed the presence in them of sterins, the alkaloid galegine, guanidine bases, and the flavonoids galuteolin and luteolin ([1,4–6]). Alkaloids and saponins have been found in the herb of this plant ([1]).

The subject of our investigations was the flowers of goat' s rue. From the flowers a flavonoid was isolated, which we have named galein. On acid hydrolysis of galein, the aglycone—galetin—was obtained. As is evident from the data in

Table 1

Properties of the flavonoids galein and galetin

Properties and qualitative reactions	Galein	Galetin	Galetin acetate
Melting point, °C	182-184°	305-307°	192-194°
Formula	$C_{27}H_{30}O_{15}$	$C_{15}H_{10}O_7$	$C_{15}H_5O_7(COCH_3)_5$
Bargellini reaction	−	+	−
Reaction with ferric chloride	greenish-brown	dark brownish-green	−
Reaction with zirconyl chloride and citric acid	−	+	−
Cyanidin reaction	+ (in water)	+ (in octanol)	+
Reaction with lead acetate	−	−	−

Properties and qualitative reactions	Galein	Galetin	Galetin acetate
Specific optical activity	−140 ($c = 1$, ethanol–pyridine 9 : 1)	0° ($c = 1$, ethanol-pyridine 9 : 1)	–
R_f in 20% acetic acid	0.70	0.05	–
Sugar component	2 molecules of rhamnose	–	–

Tables 1 and 2, galein is a glycoside containing two molecules of rhamnose. The aglycone galetin, in all probability, is a new flavonoid with five hydroxyl groups. The location of the hydroxyls in the 3, 5, 7, and 4′ positions was established by spectral investigations and confirmed by qualitative reactions, while the hydroxyl in position 6 was detected by the color qualitative Bargellini reaction ([7]). These data allowed us to propose the following formula for galetin:

(Figure: structural formula of galetin)

Galetin (3,5,6,7,4′-pentaoxyflavone) has evidently been isolated by us from nature for the first time.

Table 2

Spectral characteristics of the flavonoids galein and galetin

Solutions and reagents	A. Galein I	A. Galein II	A. Galein $\Delta\lambda$, mμ I/II	B. Galetin I	B. Galetin II	B. Galetin $\Delta\lambda$, mμ I/II	Position of phenolic hydroxyls in A and B
Solution in 96% ethanol, $2 \cdot 10^{-5}$ mole	360	265	–	375	255	–	–

Solutions and reagents	A. Galein I	A. Galein II	A. Galein $\Delta\lambda$, mμ I/II	B. Galetin I	B. Galetin II	B. Galetin $\Delta\lambda$, mμ I/II	Position of phenolic hydroxyls in A and B
Ethanolic solution + sodium acetate	360370	270	+10+5	330375	275	0+20	7+ 7+
Ethanolic solution + sodium ethylate	330400	273	+40+8	305	–	–	4′+3,4′+
Ethanolic solution + boric acid and sodium acetate	360370	265	+100	387	260	+12+5	ortho–ortho+
Ethanolic solution + aluminum chloride	355	270	+40+5	305355425	265	+50+10	5+ 5+

Solutions and reagents	A. Galein I	A. Galein II	A. Galein $\Delta\lambda$, mμ I/II	B. Galetin I	B. Galetin II	B. Galetin $\Delta\lambda$, mμ I/II	Position of phenolic hydroxyls in A and B
Ethanolic solution + aluminum chloride and hydrochloric acid	350	265	−100	360	265	+50+10	3− 3+

ones, although its partially methylated and glycosylated derivatives—pendulin[8] and fogeletin[9]—were known previously.

Comparison of the physicochemical properties of the glycoside galein and of the aglycone galetin permits the conclusion that galein is 3,6-dirhamnoside of galetin.

Isolation of galein. 2 kg of dried flowers of *Galega officinalis* are extracted with 96% ethanol. The alcoholic solution is evaporated in vacuo, the residue is treated with water, and the solution is filtered. On standing, plate-like yellow crystals separate from the aqueous filtrate, m.p. 182-184°. The substance gives positive reactions for flavonoids: the cyanidin reaction, and reactions with alkali solution, lead acetate, aluminum chloride, ferric chloride, and zirconyl chloride. Yield 1.2%.

Galetin. 1.0 g of galein is dissolved in 30 ml of 3% hydrochloric acid in 50% ethanol and hydrolyzed by heating for 30 min on a boiling water bath. Yellow needles precipitate, m.p. 305-307°. The aglycone gives positive reactions: the cyanidin reaction, the Bargellini reaction, and reactions with ferric chloride solution, lead acetate, and zirconyl chloride with citric acid.

After separation of the aglycone, the acidic hydrolysate is neutralized to pH 7 and evaporated in vacuo to dryness. The residue is treated with absolute

alcohol, filtered, and chromatographed in the systems: *n*-butanol–acetic acid–water (4 : 1 : 5) and *n*-butanol–pyridine–water (6 : 4 : 3), alongside standards of known monosaccharides. Only rhamnose was found in the hydrolysate.

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Note: Figure translations are in progress. See original paper for figures.