Phytochemistry, Vol. 27, No. 9, pp. 3017–3018, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00
© 1988 Pergamon Press plc.

QUERCETIN 3-RHAMNOSYL (1→2) GALACTOSIDE FROM *LYSIMACHIA VULGARIS* VAR. *DAVURICA**

KEN YASUKAWA and MICHIO TAKIDO

Department of Pharmacy, College of Science and Technology, Nihon University, Tokyo 101, Japan

(*Received* 22 *December* 1987)

Key Word Index—*Lysimachia vulgaris* var. *davurica*; Primulaceae; flavonol glycosides; quercetin 3-*O*-α-rhamnopyranosyl (1→2)-β-galactopyranoside.

Abstract—From the whole plant of *Lysimachia vulgaris* var. *davurica*, a new flavonol glycoside was isolated together with astragalin, hyperin, isorhamnetin 3-galactoside, syringetin 3-galactoside and isorhamnetin 3-robinobioside. The structure of the new compound was established as quercetin 3-rhamnosyl (1→2) galactoside.

INTRODUCTION

Glycosides of the flavonols kaempferol, quercetin and myricetin have already been isolated from a number of *Lysimachia* species (*L. vulgaris* [1, 2], *L. punctata* [3], *L. nummularia* [4], *L. japonica* [5], *L. clethroides* [5] and *L. mauritiana* [6]). In this paper we report the isolation and characterization of six flavonol glycosides from the whole plant of *L. vulgaris* var. *davurica*, which is used in Chinese folk medicine for the treatment of high blood pressure. Isorhamnetin 3-galactoside, syringetin 3-galactoside and isorhamnetin 3-robinobioside are reported for the first time in *Lysimachia* and quercetin 3-rhamnosyl (1→2) galactoside is a new compound.

RESULTS AND DISCUSSION

The concentrated methanol extract prepared from the air-dried whole plant of *L. vulgaris* var. *davurica* was extracted successively with ethyl acetate and *n*-butanol. Four flavonol glycosides (**1**–**4**) were isolated from the ethyl acetate fraction and a further two flavonol glycosides (**5** and **6**) from the *n*-butanol fraction by column chromatography. Compounds **1**, **2** and **3** were identified as kaempferol 3-glucoside, quercetin 3-galactoside and isorhamnetin 3-galactoside, respectively by standard procedures and direct comparison with authentic samples.

Compound **4** was characterized as syringetin 3-galactoside by acid hydrolysis to give syringetin and galactose, UV spectral analysis and ^{13}C and ^{1}H NMR.

Compound **5** was identified as isorhamnetin 3-robinobioside by acid hydrolysis to isorhamnetin, galactose and rhamnose, UV spectral analysis and ^{13}C and ^{1}H NMR. The ^{13}C NMR confirmed the presence of galactose and rhamnose units in **5**, the only significant difference from **2** being an upfield shift of 5.7 ppm for the C-6 of galactose and a downfield shift of 1.7 ppm for the C-5 of galactose (Table 1). These shifts are analogous to those reported [7] for a flavonol rhamnosyl (1→6) galactoside thus confirming the sugar linkage in **5**.

Acid hydrolysis of **6** gave quercetin, galactose and rhamnose (TLC). The ^{13}C NMR of **6** in DMSO-d_6 also confirmed that it was a quercetin glycoside. The ^{13}C NMR shifts of the aglycone part of **6** corresponded well to the shifts for quercetin, the only significant difference being an upfield shift of 2.7 ppm for the C-3. The ^{13}C NMR also showed that **6** had galactose and rhamnose units in its structure, the only significant difference from **2** being an upfield shift of 4.1 ppm for the C-2 of galactose and a downfield shift of 3.5 ppm for the C-1 of galactose (Table 1). These shifts are analogous to those reported [7] for a flavonol rhamnosyl (1→2)

Table 1. ^{13}C NMR spectral data of sugar units of compounds **2**, **5** and **6**

C		Compound 2	5	6
Galactose	1	102.6	102.4	99.1
	2	71.5	71.6	75.6
	3	73.6	73.5	74.0
	4	68.2	68.4	68.1
	5	75.9	74.2	75.8
	6	60.4	66.1	60.4
Rhamnose	1	—	100.5	100.6
	2	—	71.0	70.9
	3	—	70.6	70.7
	4	—	72.3	72.3
	5	—	68.4	68.7
	6	—	17.7	17.1

25.5 MHz, 90°, DMSO-d_6, TMS as internal standard.

*Part 3 in the series 'Studies of the Constituents of Genus *Lysimachia*'. For Part 2 see Yasukawa, K. and Takido, M. (1987) *Phytochemistry* **26**, 1224 and Part 1 see Yasukawa, K. and Takido, M. (1986) *Yakugaku Zasshi* **106**, 939.

Table 2. Flavonol glycosides of *L. vulgaris* and *L. vulgaris* var. *davurica*

Sugar unit	Kaempferol	Quercetin	Isorhamnetin	Myricetin	Syringetin
7-Glc		○			
3-Glc	○ ●	○			
3-Gal		●	●		●
3-Rha-Glc	○	○		○	
3-Rha-Gal		●	●		

Key: Glc, glucoside; Gal, galactoside; Rha-Glc, rhamnosylglucoside; Rha-Gal, rhamnosylgalactoside.
○: *L. vulgaris*; ●: *L. vulgaris* var. *davurica*.

galactoside. The structure of **6** was therefore determined as quercetin 3-*O*-α-rhamnopyranosyl (1 → 2)-β-galactopyranoside.

The flavonol glycosides for the basic species *L. vulgaris* have been isolated also and are compared with the variety *davurica* in Table 2. The two taxa show marked differences in the flavonol aglycones and glycosides present with only kaempferol 3-glucoside common to both. This may suggest that there may be more than a varietal difference between these two plants.

EXPERIMENTAL

Mps: uncorr. ^{1}H and ^{13}C NMR spectra were recorded at 100 and 25.5 MHz, respectively, chemical shifts are given in δ(ppm) with TMS at int. std. CC was carried out using Sephadex LH-20 (Pharmacia). TLC on Avicel SF (Funakoshi) was performed with *n*-BuOH–HOAc–H_2O (3:1:1).

Plant material. Lysimachia vulgaris Linn. var. *davurica* (Ledeb.) R. Kunth was collected at Mt Nyukasa, Nagano, Japan in the autumn of 1985.

Extraction and isolation. Dried whole plants (300 g) were extracted with MeOH and the concd extract macerated with hot H_2O and filtered. The H_2O soln were extracted with EtOAc followed by *n*-BuOH. Yield: EtOAc extract (2 g) and *n*-BuOH extract (3.4 g).

The EtOAc extract (2 g) was then subjected to CC on Sephadex LH-20, using MeOH as eluent, to yield **1** (15 mg), **2** (350 mg), **3** (400 mg) and **4** (90 mg). The *n*-BuOH extract (3 g) was analysed by the same method, to yield **5** (10 mg) and **6** (60 mg).

Quercetin 3-O-α-rhamnopyranosyl (1→2)-β-galactopyranoside (**6**). Recryst. (H_2O–MeCN) gave yellow needles, mp 205–207°. Analysis: calcd: $C_{27}H_{30}O_{17}$: C, 53.11; H, 4.95; found: C, 52.90; H, 5.03. Dark green with $FeCl_3$, pale red with Mg + HCl test. UV λ_{max}^{EtOH} nm: 258, 266sh, 364. ^{1}H NMR (DMSO-d_6, 90°) δ ppm: 7.65 (1H, *dd*, *J* = 1.9 Hz, *J* = 8.8 Hz, H-6'), 7.52 (1H, *d*, *J* = 1.9 Hz, H-2'), 6.82 (1H, *d*, *J* = 8.8 Hz, H-5'), 6.36 (1H, *d*, *J* = 1.9 Hz, H-8), 6.18 (1H, *d*, *J* = 1.9 Hz, H-6), 5.61 (1H, *d*, *J* = 7.3 Hz, galactosyl H-1), 5.09 (1H, *s*, rhamnosyl H-1), 0.86 (3H, *d*, *J* = 6.3 Hz, rhamnosyl Me-6). ^{13}C NMR (DMSO-d_6, 90°) δ ppm: 177.3 (C-4), 163.9 (C-7), 161.3 (C-5), 156.3 (C-2), 156.2 (C-9), 148.2 (C-4'), 144.7 (C-3'), 133.1 (C-3), 122.0 (C-1'), 121.5 (C-6'), 116.0 (C-5'), 115.3 (C-2'), 104.2 (C-10), 98.7 (C-6), 93.5 (C-8). Chemical shifts of sugar units are given in Table 1.

Hydrolysis of **6**. Compound **6** (5 mg) treated with 2 N HCl at 100° for 3 hr gave quercetin direct comparison with an authentic sample and rhamnose and galactose (TLC).

Acknowledgements—We thank Miss T. Tsukada, and Dr T. Takido, Analytical Center, College of Science and Technology, Nihon University, for elemental analysis and NMR spectra.

REFERENCES

1. Rzadkowska-Bodalska, H. and Olechnowicz-Stepien, W. (1975) *Pol. J. Pharmacol. Pharm.* **27**, 345.
2. Prum, N., Pichon, P. and Raynaud, J. (1972) *Plant. Med. Phytother.* **6**, 267.
3. Mendez, J. (1970) *Experientia* **26**, 108.
4. Popov, V. I. (1967) *Tr. Leningrad. Khim.-Farm. Inst.* **21**, 221.
5. Yasukawa, K. and Takido, M. (1986) *Yakugaku Zasshi* **106**, 939.
6. Yasukawa, K. and Takido, M. (1987) *Phytochemistry* **26**, 1224.
7. Markham, K. R., Ternai, B., Stanley, R., Geiger, H and Mabry, T. J. (1978) *Tetrahedron* **34**, 1389.