Pergamon

Phytochemistry, Vol. 48, No. 8, pp. 1445–1447, 1998

Printed in Great Britain
0031-9422/98/$—see front matter

PII: S0031-9422(97)01025-X

FLAVONOL GLYCOSIDES FROM *LYSIMACHIA CONGESTIFLORA*

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(*Received in revised form* 16 *October* 1997)

Key Word Index—*Lysimachia congestiflora*; Primulaceae; flavonol glycoside; larycitrin 3-*O*-α-arabinofuranoside; syringetin 3-*O*-α-rhamnopyranosyl(1 → 5)-α-arabinofuranoside.

Abstract—Two new flavonol glycosides, larycitrin 3-*O*-α-arabinofuranoside and syringetin 3-*O*-α-rhamnopyranosyl(1 → 5)-α-arabinofuranoside, together with syringetin and six known flavonol glycosides, kaempferol 3-*O*-α-arabinofuranoside, myricetin 3-rhamnoside and 3-*O*-arabinofuranoside, syringetin 3-*O*-α-arabinofuranoside and 3-rhamnoside, and larycitrin 3-rhamnoside were isolated from the whole plant of *Lysimachia congestiflora*. All structures were established on the basis of UV, MS and NMR spectral analyses. © 1998 Published by Elsevier Science Ltd. All rights reserved

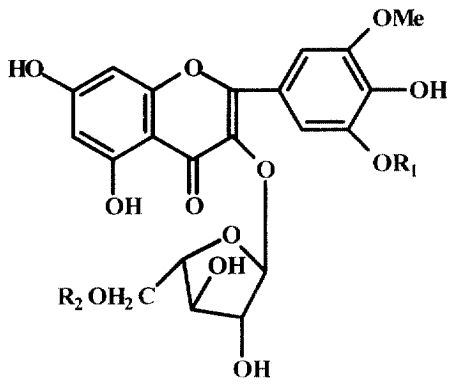
INTRODUCTION

Glycosides of kaempferol, quercetin, myricetin and syringetin have been isolated previously from *Lysimachia* species [1–9]. *Lysimachia congestiflora* Hemsl. is an important medicinal herb in China [10]. In the present study of its chemical constituents, one flavonol aglycone and eight flavonol glycosides, including two new compounds (**1** and **2**) have been isolated and characterized.

RESULTS AND DISCUSSION

The concentrated ethanolic extract of the air-dried whole plant of *L. congestiflora* was eluted successively with chloroform, ethyl acetate, acetone and methanol under reflux in a Soxhlet. One flavonol and eight flavonol glycosides (**1**–**9**) were isolated from the acetone fraction. The known flavonol glycosides: kaempferol 3-*O*-α-arabinofuranoside (**3**), myricetin 3-rhamnoside (**4**) and 3-*O*-α-arabinofuranoside (**5**), syringetin 3-*O*-arabinofuranoside (**6**) [11] and 3-rhamnoside (**7**) [12], and larycitrin 3-rhamnoside (**8**) [12], and free syringetin (**9**) [11] were characterized by standard procedures. Among them, **3**, **6**, **7** and **8** are reported for the first time in the genus *Lysimachia*.

Compound **1**, gave positive Mg–HCl and Molish tests. The FAB mass gave a quasi-molecular ion $[M+H]^+$ at *m/z* 465, in good agreement with the molecular formula $C_{21}H_{20}O_{12}$. UV, EI-MS and ^1H



	R_1	R_2
1	H	H
2	Me	α-*L*-rhamnopyranosyl

NMR spectral analyses indicated that the aglycone of **1** was larycitrin, the 3′-methyl ether or myricetin. In the NOESY experiment, the methoxyl group (δ 3.85) gave an NOE interaction with H-2′ (δ 7.31), further supporting the presence of larycitrin. The FAB mass spectrum of **1** exhibited a quasi-molecular ion $[M+H]^+$ at *m/z* 465 and $[M+H-132]^+$ at *m/z* 333, suggesting the presence of a pentose sugar. Acid hydrolysis of **1** yielded arabinose. The ^{13}C NMR of **1** in DMSO-d_6 also confirmed that **1** was a glycoside of larycitrin. The only significant difference was an

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Table 1. ^{1}H NMR Chemical shifts for compounds **1** and **2** (400 MHz, DMSO-d_6, TMS as internal standard)

Position	1	2
H-6	6.21 (*d*, 2.0 Hz)	6.22 (*d*, 2.0 Hz)
H-8	6.43 (*d*, 2.0 Hz)	6.50 (*d*, 2.0 Hz)
H-2′	7.31 (*d*, 1.9 Hz)	7.34 (*s*)
H-6′	7.17 (*d*, 1.9 Hz)	7.34 (*s*)
OCH_3	3.85 (*s*)	3.86 (*s*, $OCH_3 \times 2$)
H-1″ (ara.)	5.61 (*d*, $J = 0.9$ Hz)	5.58 (*d*, 0.8 Hz)
H-1‴ (rha.)		4.39 (*d*, 1.1 Hz)

upfield shift of 2.6 ppm for the C-3 (δ 133.4). This shift was analogous to that reported for flavonols in which the 3-hydroxyl group was glycosylated [13, 14]. The UV shifts on the addition of sodium methoxide and aluminum chloride also indicated that the position of linkage between the sugar and aglycone was at C-3. In addition, ^{13}C NMR data for the sugar were in accord with those for methyl-α-L-arabinofuranoside, reported in the literature [15]. Thus, **1** was identified as larycitrin 3-*O*-α-arabinofuranoside, a new flavonol glycoside.

Compound **2**, gave positive Mg–HCl and Molish tests. The FAB-MS gave a quasi-molecular ion $[M+H]^+$ at *m/z* 625, corresponding with the molecular formula $C_{28}H_{32}O_{16}$. UV, EI-MS and NMR analyses indicated that the aglycone of **2** was 5,7,4′-trihydroxy-3′,5′-dimethyoxylflavonol, namely syringetin. The FAB-MS exhibited a quasi-molecular ion $[M+H]^+$ at *m/z* 625 and other significant peaks at *m/z* 479 $[M+H-146]^+$ and 347 $[M+H-146-132]^+$, corresponding to the successive loss of one deoxyhexosyl and one pentosyl moiety. Acid hydrolysis of **2** yielded rhamnose and arabinose. The ^{13}C NMR of **2** in DMSO-d_6 also confirmed that it was a glycoside of syringetin, the only significant differences were an upfield shift of 2.7 ppm for C-3 and a downfield shift of 10 ppm for C-2, indicating that the position of linkage between the sugar and aglycone was at C-3. The ^{13}C NMR spectrum also showed that **2** had rhamnose and arabinose in its structure, the significant differences were an upfield shift of 1.5 ppm for C-4 and a downfield shift of 2.7 ppm for C-5 of arabinose (Table 1) compared with data for methyl-α-L-arabinofuranoside reported in the literature [15], suggesting that the arabinose was the inner sugar and the rhamnose was attached to C-5 of the arabinose. Therefore, the structure of **2** was identified as syringetin 3-*O*-α-rhamnopyranosyl(1 → 5)-α-arabinofuranoside, another new flavonol glycoside.

EXPERIMENTAL

General

Mps are uncorr. ^{1}H and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively, in DMSO-d_6 using TMS as int. standard. Chemical shifts are expressed in δ values.

Plant material

Lysimachia congestiflora Hemsl. was obtained from Jiang Kou, Guizhou province, China in 1990, and identified by Associate Professor Baolin Guo of this institute. A voucher specimen has been deposited in

Table 2. ^{13}C NMR Chemical shifts for compounds **1**, **2** and **9** (100 MHz, DMSO-d_6, TMS as internal standard)

position	1	2	9	Position	1	2
2	156.4	156.4	146.4	ara. C-1″	107.7	107.8
3	133.4	133.3	136.0	C-2″	82.5	82.7
4	177.7	177.6	175.8	C-3″	76.9	77.3
5	161.3	161.2	160.0	C-4″	85.6	83.3
6	98.6	98.7	98.2	C-5″	60.4	65.2
7	164.2	164.2	163.9	rha. C-1‴		99.8
8	93.6	94.0	93.7	C-2‴		70.2
9	156.9	157.1	156.1	C-3‴		70.5
10	103.9	104.0	103.0	C-4‴		71.8
1′	119.8	119.7	120.8	C-5‴		68.3
2′	109.5	106.6	105.8	C-6‴		17.7
3′	147.8	147.5	147.7			
4′	137.4	138.6	138.1			
5′	145.7	147.5	147.7			
6′	105.6	106.6	105.8			
OCH_3	55.8	56.0	56.2			

the Herbarium of the Institute of Medicinal Plant Development.

Extract and isolation

Dried whole plants of *L. congestiflora* (18 kg) were extracted with EtOH and the concd extract eluted with $CHCl_3$, EtOAc, Me_2CO and MeOH, respectively under reflux in a Soxhlet. The Me_2CO fraction (100 g) was subjected to CC on polyamide, using $CHCl_3$–MeOH as eluant, and then subjected to CC on sephadex LH-20, using MeOH as eluant, yielding **1** (31 mg), **2** (40 mg), **3** (17 mg), **4** (105 mg), **5** (34 mg), **6** (25 mg), **7** (150 mg), **8** (606 mg), **9** (30 mg).

Larycitrin 3-O-α-arabinofuranoside (**2**). Recrystallization (MeOH–H_2O) gave a pale yellow amorphous powder, mp 178–180°. Compound **1** gave a pale red colour in the Mg–HCl test. UV λ_{max}^{MeOH}: 250, 300 (sh), 354; +MeONa 266, 314, 400; +$AlCl_3$ 270, 300, 430; +AlCl+HCl 270, 300, 360, 396; +NaOAc 266, 320 (sh), 386; +H_3BO_3 260, 300, 378 nm. EI-MS *m/z* (%): 332 (100), 317 (5), 303 (10), 261 (5), 167 (2), 153 (12), 69 (10), 44 (5). FAB-MS *m.z* (%): 465 $[M+1]^+$, 333 $[M+1-167$ (2), 153 (12), 69 (10), 44(5). FAB-MS *m/z* (%): 465 $[M+1]^+$, 333 $[M+1-132]^+$, 332 $[M-132]^+$, 317 $[M+1-132-15]^-$. ^1C NMR see Tables 1 and 2.

Syringetin 3-O-α-rhamnopyranosyl(1 → 5)-α-arabinofuranoside (**2**). Recrystallization of **2** (MeOH–H_2O) gave a pale yellow amorphous powder, mp 284–286°. It gave a pale red colour with Mg–HCl. UV λ_{max}^{MeOH}: 252, 262, 300, 254; +NaOMe 266, 325, 420; +$AlCl_3$ 266, 310 (sh), 360 (sh), 405; +$AlCl_3$+HCl 266, 310, 360, 405; +NaOAc, 274, 320, 390; +H_3BO_3 266, 354. EI-MS *m/z* (%): 346 (100), 317 (5), 287 (2), 216 (5), 181 (2), 153 (10), 136 (5), 60 (15). FAB-MS *m/z* (%): 625 $[M+1]^+$, 479 $[M+1-146]^+$, 347 $[M+1-146-132]^+$, 346 $[M-146-132]^+$. For ^1H NMR and ^{13}C NMR see Table 1 and Table 2.

Acknowledgments—We thank Mr Lu Mu-Jian (Analytical center, Peking University) for NMR spectra.

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