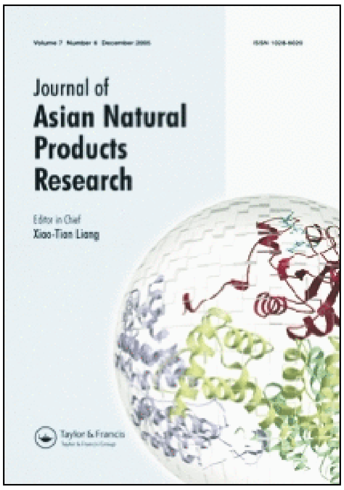

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Two new phenylpropanoid esters of rhamnose from *Lagotis yunnanensis*

Xiao-Dong Yang[a]; Zi-Yan Li[b]; Shuang-Xi Mei[a]; Jing-Feng Zhao[a]; Hong-Bin Zhang[a]; Liang Li[a]
[a] School of Pharmacy, Yunnan University, Kunming [b] School of Environmental Science and Engineering, Knuming University of Science and Technology, Kunming, China

To cite this Article Yang, Xiao-Dong , Li, Zi-Yan , Mei, Shuang-Xi , Zhao, Jing-Feng , Zhang, Hong-Bin and Li, Liang(2003) 'Two new phenylpropanoid esters of rhamnose from *Lagotis yunnanensis*', Journal of Asian Natural Products Research, 5: 3, 223 — 226

To link to this Article: DOI: 10.1080/1028602031000093366

URL: http://dx.doi.org/10.1080/1028602031000093366

Journal of Asian Natural Products Research, 2003 VOL. 5 (3), pp. 223–226

TWO NEW PHENYLPROPANOID ESTERS OF RHAMNOSE FROM *LAGOTIS YUNNANENSIS*

XIAO-DONG YANG[a], ZI-YAN LI[b], SHUANG-XI MEI[a], JING-FENG ZHAO[a],
HONG-BIN ZHANG[a] and LIANG LI[a,*]

[a]*School of Pharmacy, Yunnan University, 2 North Cui Hu Road, Kunming 650091, China;* [b]*School of Environmental Science and Engineering, Knuming University of Science and Technology, 86 Wenchang Road, Kunming 650093, China*

(Received 29 October 2002; Revised 19 December 2002; In final form 6 January 2003)

Two new phenylpropanoid esters of rhamnose, lagotoside B (**1**) and lagotoside C (**2**), together with three known compounds (**3**–**5**), were isolated from *Lagotis yunnanensis*. The structures of **1** and **2** were elucidated by spectroscopic methods. Compounds **3**–**5** have been obtained from this species for the first time.

Keywords: Scrophulariaceae; *Lagotis yunnanensis*; Phenylpropanoids; Lagotoside B; Lagotoside C

INTRODUCTION

The genus *Lagotis* (Scrophulariaceae) is represented with 17 species in China, mostly growing in the southwestern part of the country on mountains of 3000 m above sea level or higher [1]. Several species, such as *L. glauca*, *L. integra*, *L. brachystachya* and *L. yunnanensis*, are used in Tibetan folkloric medicine for the treatment of fever, high blood pressure and acute and chronic hepatitis [2,3]. In the literature, the chemical compositions of two species of *Lagotis* have been studied. Flavonoids were isolated from *L. brachystachya* [4], while phenylpropanoid glucosides and iridoid glucosides were found in *L. stolonifera* [5]. As part of our studies of medicinal plants growing on the Yunnan-Tibet Plateau, *L. yunnanensis* W. W. Smith has been examined. To the best of our knowledge, no scientific study on this plant has hitherto been reported. Two new phenylpropanoid esters of rhamnose, lagotoside B (**1**) and lagotoside C (**2**) (Fig. 1), together with three known flavones, 5,7,4′-trihydroxy-3′,5′-dimethoxyflavone (**3**) [6], chrysoeriol (**4**) [4] and apigenin (**5**), were isolated from the title plant.

---

*Corresponding author. Tel.: +86-871-5033644. Fax: +86-871-5035538. E-mail: Liliang5758@sina.com

ISSN 1028-6020 print/ISSN 1477-2213 online
DOI: 10.1080/1028602031000093366

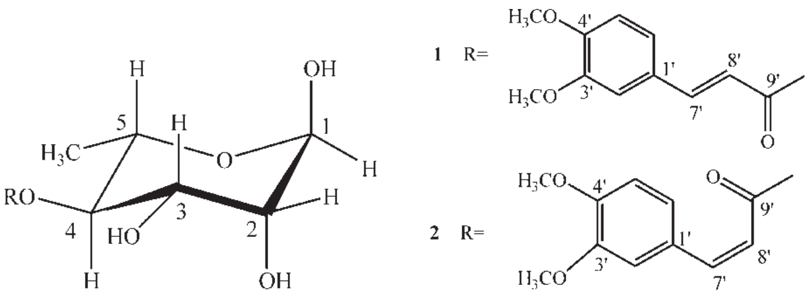

FIGURE 1 Structures of **1** and **2**.

RESULTS AND DISCUSSION

Lagotoside B (**1**) was isolated as a pale yellow amorphous powder. Its molecular formula was determined as $C_{17}H_{22}O_8$ by HREIMS. The IR spectrum showed characteristic absorptions for OH (3367 cm^{-1}, br), α,β-unsaturated ester (1690 and 1630 cm^{-1}), and aromatic-ring (1598, 1559 and 1508 cm^{-1}). The UV spectrum at 232 (3.70), 265 (3.22) and 320 (3.84) nm also confirmed the existence of these unsaturated functional groups. From its NMR data (Table I), the signals of a (*E*)-3,4-disubstituted-cinnamoyl (C-1′ to C-9′, H-2′, H-5′, H-6′, H-7′ and H-8′) and an α-L-rhamnose (C-1 to C-6, H-1 to H-6) were observed. The ^1H NMR spectrum showed two olefinic protons for a *trans* double bond (δ 7.62, 6.42, d, $J = 15.9$ Hz, H-7′, 8′), an ABX system for three aromatic protons at δ 6.99 (d, $J = 8.3$ Hz, H-6′), 7.19 (dd, $J = 2.0$, 8.3 Hz, H-5′), 7.30 (d, $J = 2.0$ Hz, H-2′) and two aromatic methoxyl groups at δ 3.88 and 3.85 (s, OCH_3). An anomeric proton at δ 5.06 (d, $J = 2.1$ Hz, H-1) and a methyl group δ 1.23 (d, $J = 6.2$ Hz, H-6) in the ^1H NMR spectrum, as well as ^{13}C NMR signals at δ 95.6 (C-1) and 18.4 (C-6) suggest the presence of a rhamnose moiety. Based on its coupling constant of anomeric proton ($J = 2.1$ Hz), an α-rhamnose was confirmed. For a β-rhamnose, the coupling constant normally appears at approximately 4.2 Hz [7]. Detailed NMR data are presented in Table I. In HMBC spectrum (Fig. 2), the correlations between δ_H 3.85 (OCH_3)

TABLE I ^1H (500 MHz) and ^{13}C NMR (125 MHz) data of **1** and **2** in $(CD_3)_2CO$, (δ in ppm)

	1		**2**	
No.	^{13}C	^1H *(J, Hz)*	^{13}C	^1H *(J, Hz)*
1	95.6 d	5.06 d (2.1)	94.6 d	5.06 d (2.1)
2	71.2 d	4.04 dd (2.1, 3.0)	70.8 d	4.03 dd (2.1, 3.0)
3	70.7 d	3.69 dd (3.0, 9.7)	70.5 d	3.67 dd (3.0, 9.7)
4	75.6 d	5.16 t (9.7)	75.6 d	5.14 t (9.7)
5	69.2 d	3.94 m	69.1 d	3.93 m
6	18.4 q	1.23 d (6.2)	18.3 q	1.22 d (6.2)
1′	128.4 s		128.7 s	
2′	111.1 d	7.30 d (2.0)	115.1 d	7.85 d (2.0)
3′	150.7 s		149.6 s	
4′	152.6 s		151.6 s	
5′	111.8 d	6.99 d (8.3)	111.9 d	6.93 d (8.4)
6′	123.6 d	7.19 dd (2.0, 8.3)	126.0 d	7.33 dd (2.0, 8.4)
7′	145.2 d	7.62 d (15.9)	143.8 d	6.87 d (13.0)
8′	117.1 d	6.42 d (15.9)	118.0 d	5.87 d (13.0)
9′	167.3 s		166.7 s	
OCH_3	56.2 q	3.88 s	56.1 q	3.83 s
OCH_3	56.2 q	3.85 s	56.0 q	3.80 s

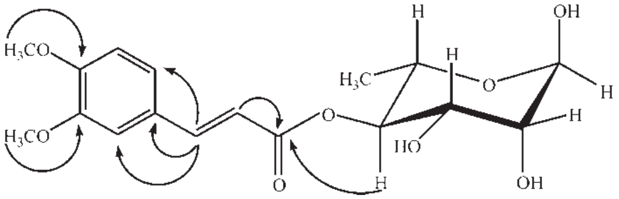

FIGURE 2 Key correlations in the HMBC spectrum of **1**.

to δ_C 150.7 (C-3′) and δ_H 3.88 (OCH_3) to δ_C 152.6 (C-4′) suggest that the cinnamoyl is (*E*)-3,4-dimethoxycinnamoyl, while δ_H 5.16 (H-4) to δ_C 167.3 (C-9′) indicate that a (*E*)-3,4-dimethoxycinnamoyl group is attached to the C-4 position of the rhamnose. Therefore, the structure of **1** was elucidated as 4-*O*-(*E*)-3′,4′-dimethoxycinnamoyl-α-L-rhamnopyranose.

Lagotoside C (**2**) was found to have the same molecular formula, determined by HREIMS, as that of **1**. Other spectroscopic data were also similar to those of **1**, except for the coupling constants of two olefinic protons, δ_H 5.87 (d, $J = 13.0\,\text{Hz}$, C-8′) and 6.87 (d, $J = 13.0\,\text{Hz}$, C-7′), from which a *cis*-form of the double bond in the acyl moiety was assumed (Fig. 3). Therefore, the structure of **2** was elucidated as 4-*O*-(*Z*)-3′,4′-dimethoxycinnamoyl-α-L-rhamnopyranose.

In addition to the two new constituents, compounds **3**–**5** were isolated from this species for the first time. Their structures were identified by direct comparison with an appropriate reference sample, or by comparing their physical and spectral data with those reported in the literature.

EXPERIMENTAL

General Experimental Procedures

UV spectra were determined on a UV 210A spectrometer and IR spectra on a Bio-Rad FTS-135 spectrometer. Both 1D and 2D NMR spectra were taken on a DRX-500 instrument with TMS as internal reference. EIMS were recorded on a VG Auto spec-3000 mass spectrometer. Preparative HPLC was performed with a Waters 600 pump connected to a 2467 tunable absorbance detector, using a Waters C_{18} column (10 × 250 mm, Millipore, USA).

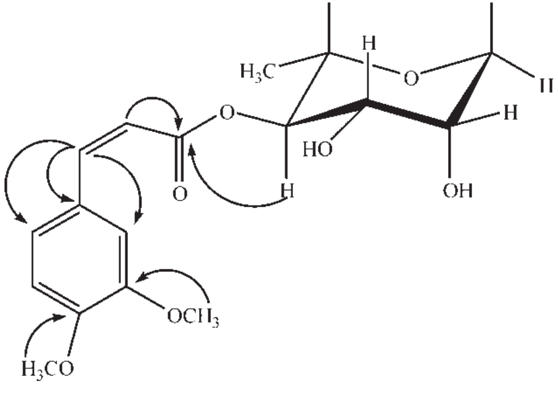

FIGURE 3 Key correlations in the HMBC spectrum of **2**.

Plant Material

The plant material was collected in Deqin Country, Yunnan Province, China, in September 2001, and identified as *Lagotis yunnanensis* W. W. Smith by Mr A. Dou (Deqin Tibetan hospital). A voucher specimen was deposited in the Department of Phytochemistry, School of Pharmacy, Yunnan University.

Extraction and Isolation

The dried whole plants (8 kg) were extracted four times with 95% EtOH (4 × 20 l) at room temperature for 9 days, and the combined extracts were then concentrated *in vacuo*. The residue was suspended in H_2O, and then partitioned with $CHCl_3$ (4 × 1.5 l) and *n*-BuOH (6 × 1.5 l), successively. The *n*-BuOH extract (897.83 g) was subjected to chromatography over silica gel (1.5 kg, 200–300 mesh), eluting with $CHCl_3$–MeOH–H_2O (8:1:0.1, 6:1:0.1, 4:1:0.15, 2:1:0.2, 1:1:0.4 and 0:1:0), to afford seventeen fractions (A–Q).

Fraction B (15.33 g) was purified by polyamide column chromatography eluted with $CHCl_3$–MeOH (1:0–0:1) to give two fractions (1 and 2). Fr. 1 was rechromatographed by HPLC (MeOH–H_2O 35:65, 8 ml min^{-1}, UV detector, 320 nm) to yield compound **2** (t_R 340–355 ml, 6 mg) and **1** (t_R 370–400 ml, 15 mg); Fr. 2 was purified by silica gel column chromatography eluted with $CHCl_3$–MeOH (30:1) to give compounds **3** (862 mg), **4** (3.6 g) and **5** (1.0 g).

Lagotoside B (**1**), $C_{17}H_{22}O_8$, pale yellow amorphous powder. UV (MeOH) λ_{max} (nm) (log ϵ) 233 (3.70), 265 (3.22), 321 (3.84); IR (film) ν_{max} (cm^{-1}): 3367, 2982, 2948, 2834, 2527, 2053, 1690, 1630, 1598, 1559, 1508, 1454, 1419, 1115, 1033, 656; ^1H and ^{13}C NMR data, see Table I; EIMS (70 eV) *m/z* 354 $[M]^+$ (19), 208 $[M-rha]^+$ (100), 191$[M-rha-H_2O+H]^+$ (95), 163 (10), 147 (9), 133 (10), 119 (9), 105 (7), 91(13), 77 (18); HREIMS *m/z* 354.1346 (calcd. for $C_{17}H_{22}O_8$: 354.1315).

Lagotoside C (**2**), $C_{17}H_{22}O_8$, pale yellow amorphous powder. IR (film) ν_{max} (cm^{-1}): 3368, 2982, 2950, 2834, 2527, 2053, 1700, 1630, 1600, 1559, 1510, 1454, 1419, 1117, 1033, 658; ^1H and ^{13}C NMR data, see Table I; EIMS (70 eV) *m/z* 354 $[M]^+$ (15), 208 $[M-rha]^+$ (100), 191$[M-rha-H_2O+H]^+$ (96), 163 (10), 147 (11), 133 (9), 119 (8), 105 (7), 103 (12), 91(13), 77 (20); HREIMS *m/z* 354.1352 (calcd. for $C_{17}H_{22}O_8$: 354.1315).

Acknowledgements

This work was supported by funds from the Unida Research Institute of the Unida Company. We are grateful to the faculty of the instrument group of Kunming Institute of Botany, Chinese Academy of Sciences for the measurement of all the spectra, and to Mr A. Dou for the identification of the plant material.

References

[1] Institute of Botany, Chinese Academy of Sciences (1979), *Flora Reipublicae Popularis Sinicae* (Science Press, Beijing) Vol. 67, Part 2, pp. 325–343.
[2] Gansu Health Bureau (1974), *Handbook of Traditional Chinese Medicines in Gansu* (Gansu People Press, Lanzhou), pp. 121–122.
[3] Yunnan Medicinal Material Company (1993), *Index Chinese Medicines Resources Yunnanensis* (Science Press, Beijing), pp. 486–487.
[4] Chen, Y.Z., Zhang, H.D., Zhang, S.M. and Yang, Q.H. (1989), *Chem. J. Chin. Univer.* **10**, 260–262.
[5] Ihsan, C., Deniz, T., Anthomy, D.W. and Otto, S. (1991), *Helv. Chim. Acta* **74**, 1273–1277.
[6] Pawan, K.A. and Ram, P.R. (1981), *Heterocycles* **61**, 2181–2236.
[7] Yue, J.M., Chen, S.N., Yang, S.P., Fan, C.Q., Lin, Z.W. and Sun, H.D. (2001), *Acta Bot. Sin.* **43**, 1199–1201.