Chinese Chemical Letters Vol. 15, No. 1, pp 49– 51 , 2004
http://www.imm.ac.cn/journal/ccl.html

Two New Iridoid Glucosides from *Lagotis yunnanensis*

Xiao Dong YANG, Jing Feng ZHAO, Shuang Xi MEI, Jian Xin PU,
Hong Bin ZHANG, Liang LI*

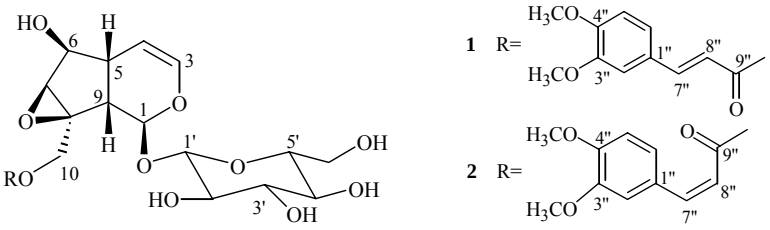
School of Pharmacy, Yunnan University, Kunming 650091

Abstract: Two new iridoid glucosides **1** and **2**, 10-*O*-(3, 4-dimethoxy-(*E*)-cinnamoyl)catalpol and 10-*O*-(3, 4-dimethoxy-(*Z*)-cinnamoyl)catalpol, were isolated from *Lagotis yunnanensis*. Their structures were elucidated by spectroscopic methods.

Keywords: *Lagotis yunnanensis*, iridoid glucosides, 10-*O*-(3, 4-dimethoxy-(*E*)-cinnamoyl)catalpol, 10-*O*-(3, 4-dimethoxy-(*Z*)-cinnamoyl)catalpol.

In the previous papers[1, 2], we reported some chemical constituents from *Lagotis yunnanensis* W. W. Smith. A continuation of our studies on the same plant led to the isolation of an *E*/*Z*-mixture of two new iridoid glucosides, 10-*O*-(3, 4-dimethoxy-(*E*/*Z*)-cinnamoyl)catalpol (**1**/**2**). Herein we reported their structures as well as their spectral data.

Figure 1 The structures of **1** and **2**

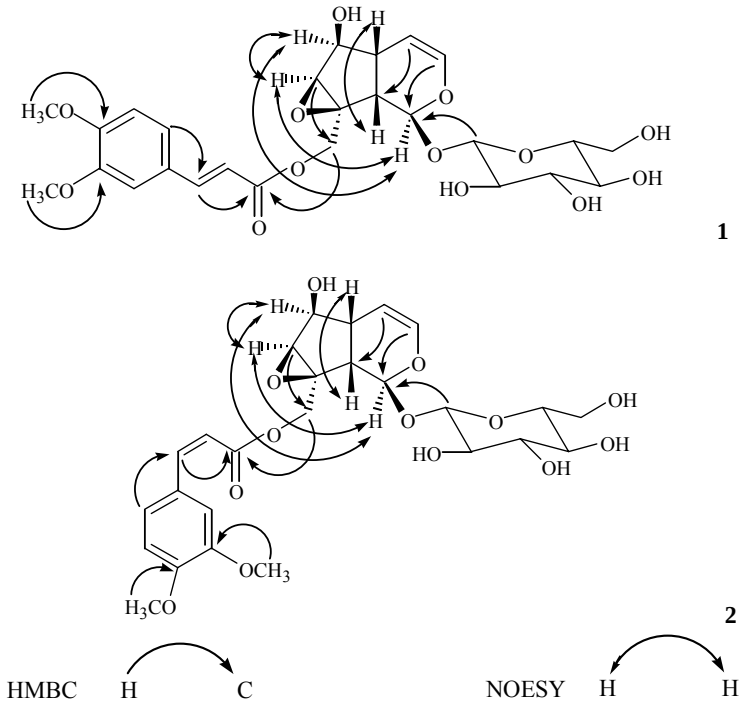


Compound **1** and **2** were isolated as an inseparable mixture of *E*/*Z*-isomers in the proportion of 2:1. Their molecular formulas were determined as $C_{26}H_{32}O_{13}$ by HRFABMS (found 552.1838, calcd. 552.1843). The negative FABMS spectrum displayed a series of fragment ion: *m/z* 552 $[M]^+$ (3.6), 390 $[M\text{-}Glu]^+$ (5.1), 353 (3.0), 268 (4.2), 207 $[C_6H_3(OMe)_2CH{=}CH\text{-}COOH\text{-}1]^+$ (100), 191 (87.5), 182 (30.4), 164 (56.7), 147 (45.2). The IR spectrum showed characteristic absorptions for OH (3367 cm^{-1}, br), *α*, *β*-unsaturated ester (1700 and 1630 cm^{-1}), and aromatic carbon carbon double band (1598 and 1508 cm^{-1}). The UV absorption at 230, 294 and 321 nm also confirmed the existence of these unsaturated functional groups. The NMR spectrum (**Table 1**) demonstrated that the compounds were ester of catalpol[3]. Besides a partly doubled set

* E-mail: liliang5758@sina.com

of signals from an iridoid similar to catalpol (C_1, C_3 to C_{10} and $C_{1'}$ to $C_{6'}$; H_1 to H_7, H_9, H_{10} and $H_{1'}$ to $H_{6'}$), additional doubled signals arising from an *E*/*Z*-mixture of 3, 4-dimethoxycinnamoyl moieties ($C_{1''}$ to $C_{9''}$; $H_{2''}$, $H_{5''}$, $H_{6''}$, $H_{7''}$, $H_{8''}$ and 2×OCH_3) could be seen. The ^{13}C NMR data of **1** and **2** correlated well with the reported data for 6-*O*-(3, 4-dimethoxy-(*E*/*Z*)-cinnamoyl)cotalpol[4], as well as the mixture of *E*/*Z*-isomers, thus indicating a close structural resemblance between **1**/**2** and 6-*O*-(3, 4-dimethoxy-(*E*/*Z*)-cinnamoyl)cotalpol. Upfield shifts of 1.91, 3.21 ppm and downfield shifts of 1.88, 3.05 ppm were observed for C_6, C_8 and C_7, C_{10} signals, respectively. Except for these shifts, the ^{13}C NMR spectral patten of **1** and **2** were almost identical with that of 6-*O*-(3, 4-dimethoxy-(*E*/*Z*)-cinnamoyl)cotalpol. The difference of chemical shifts of C_6, C_8, C_7 and C_{10} signals in the compound **1/2** and 6-*O*-(3, 4-dimethoxy-(*E*/*Z*)-cinnamoyl) cotalpol

Figure 2 The key correlations in HMBC and NOESY spectrum of **1** and **2**



were induced by the different substituent positions of 3, 4-dimethoxy-(*E*/*Z*)- cinnamoyl. In HMBC spectrum (**Figure 2**), the obvious correlations of δ_H 4.98 and 4.25/4.74 and 4.20 (H-10) to δ_C 168.79/167.86 (C-9″) indicated that 3, 4-disubstituted- (*E*/*Z*)-cinnamoyl was substituted at C-10 position, while δ_H 3.86/3.85 (OCH_3) to δ_C 150.80/149.75 (C-3″) and δ_H 3.87/3.85 (OCH_3) to δ_C 152.91/151.76 (C-4″) suggested that the cinnamoyl is 3, 4-dimethoxy-(*E*/*Z*)-cinnamoyl. NOESY experiments were also conducted and the key correlations are indicated in **Figure 2**. The correlations between H_1 and H_6, H_1 and H_7, H_6 and H_7 as well as H_5 and H_9 suggested that the relative configuration of C_1, C_6, C_7, C_5 and C_9 in compound **1** and **2** were similar to that of catalpol. Therefore, compound **1** and **2** were elucidated as 10-*O*-(3, 4-dimethoxy-(*E*/*Z*)- cinnamoyl)cotalpol.

Table 1 ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) data of **1** and **2** in CD_3OD, (δ in ppm)

	1		**2**	
C	δ_C	δ_H (*J*, Hz)	δ_C	δ_H (*J*, Hz)
1	95.62 (d)	5.05 (d, 1H, 9.2)	95.62 (d)	5.03 (d, 1H, 9.2)
3	141.81 (d)	6.36 (dd, 1H, 6.0, 1.8)	141.81 (d)	6.34 (dd, 1H, 6.0, 1.8)
4	103.73 (d)	5.08 (dd, 1H, 6.0, 4.9)	103.73 (d)	5.07 (dd, 1H, 6.0, 4.9)
5	37.42 (d)	2.66 (m, 1H)	37.42 (d)	2.66 (m, 1H)
6	79.49 (d)	3.95 (dd, 1H, 7.9, 1.2)	79.49 (d)	3.93 (dd, 1H, 7.9, 1.2)
7	62.80 (d)	3.64 (br, s, 1H)	62.80 (d)	3.64 (br, s, 1H)
8	63.59 (s)		63.59 (s)	
9	43.67 (d)	2.98 (dd, 1H, 9.2, 7.7)	43.67 (d)	3.01 (dd, 1H, 9.2, 7.7)
10	64.35 (d)		64.35 (d)	
10a		4.25 (d, 1H, 12.8)		4.20 (d, 1H, 12.7)
10b		4.98 (d, 1H, 12.8)		4.94 (d, 1H, 12.7)
1′	100.32 (d)	4.75 (d, 1H, 7.8)	100.32 (d)	4.74 (d, 1H, 7.8)
2′	74.84 (d)	3.21 (dd, 1H, 9.1, 7.8)	74.84 (d)	3.19 (dd, 1H, 9.1, 7.8)
3′	78.53 (d)	3.42 (dd, 1H, 9.1, 8.4)	78.53 (d)	3.40 (dd, 1H, 9.1, 8.4)
4′	71.48 (d)	3.17 (dd, 1H, 10.0, 8.4)	71.48 (d)	3.16 (dd, 1H, 10.0, 8.4)
5′	77.88 (d)	3.38 (m, 1H)	77.88 (d)	3.38 (m, 1H)
6′	63.03 (s)		63.03 (s)	
6′a		3.64 (dd, 1H, 11.9, 6.0)		3.62 (dd, 1H, 11.9, 6.0)
6′b		3.92 (dd, 1H, 11.9, 2.0)		3.90 (dd, 1H, 11.9, 2.0)
1″	128.85 (s)		129.22 (s)	
2″	111.70 (d)	7.32 (d, 1H, 1.9)	112.13 (d)	7.70 (d, 1H, 1.9)
3″	150.80 (s)		149.75 (s)	
4″	152.91 (s)		151.76 (s)	
5″	112.67 (d)	7.19 (dd, 1H, 8.4, 1.9)	114.98 (d)	6.94 (d, 1H, 8.4)
6″	124.10 (d)	6.98 (d, 1H, 8.4)	126.17 (d)	7.12 (dd, 1H, 8.4, 1.9)
7″	146.70 (d)	7.66 (d, 1H, 16.0)	145.23 (d)	6.91 (d, 1H, 12.9)
8″	116.25 (d)	6.45 (d, 1H, 16.0)	117.48 (d)	5.88 (d, 1H, 12.9)
9″	168.70 (s)		167.86 (s)	
OCH_3	56.71 (q)	3.87 (s, 3H)	56.44 (q)	3.85 (s, 3H)
	56.55 (q)	3.86 (s, 3H)	56.37 (q)	3.85 (s, 3H)

Acknowledgment

This work was supported by the Natural Science Foundation of Yunnan Education Department (No. 02ZY018) and Natural Science Foundation of Yunnan University (No. 2002Q005YY), which are grateful acknowledged.

References

1. X. D. Yang, S. X. Mei, J. F. Zhao, G. P. Li, H. B. Zhang, L. Li, *Chin. Chem. Lett.* (in press).
2. X. D. Yang, S. X. Mei, R. Yang, J. X. Pu, J. F. Zhao, L. Li, *Natural Product Research and Development*, **2002**, *14* (6), 1.
3. R. K. Chaudhuri, O. Sticher, *Helv. Chim. Acta*, **1981**, *64* (1), 3.
4. O. A. Ekabo, N. P. Farnsworth, T. Santisuk, V. Reutrakul, *Phytochemistry*, **1993**, *32* (3),747.

Received 10 December, 2002