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β-Carboline monoterpenoid glucosides from *Palicourea adusta*☆

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Abstract

Lyaloside, a monoterpenoid glucoindole alkaloid, was isolated from the leaves of *Palicourea adusta* together with a mixture of its hydroxycinnamic acid derivatives, (*E*)-*O*-(6′)-cinnamoyl-4″-hydroxy-3″-methoxy-lyaloside and (*E*)-*O*-(6′)-cinnamoyl-4″-hydroxy-3″,5″-dimethoxy-lyaloside, which have been separated for the first time by high pressure liquid chromatography (HPLC). Their molecular weights were determined by HPLC electrospray ionization mass spectrometry (ESI-MS) and further identification of the structures was carried out by spectroscopic methods.

Keywords: *Palicourea adusta*; Rubiaceae; β-carboline; Lyaloside; Cinnamic acid derivatives

1. Introduction

Palicourea adusta Standley is a small shrub, recognized by its small leaves and usually bluish flowers. The species grows only in the region from the Cordillera de Tilarán, Costa Rica to western Panama. The occurrence of β-carboline monoterpenoids glucosides in the genus *Palicourea* is well documented. Analogous indole alkaloids with secologanin moieties have already been detected in the leaves of *P. marcgravii* as palicoside (Morita et al., 1989) and in *P. alpina* as the alkaloid palinine (Stuart & Woo-Ming, 1974). There are also reports of the occurrence of lyaloside (**1**) in some species of the genera *Ophiorrhiza* sp. (Aimi, Seki & Sakai, 1992) and *Pauridiantha* sp. (Levesque, Pousset & Cavé, 1975) (both Rubiaceae). A hydroxycinnamic acid derivative of **1** was found in *Cephaelis axillaris* (Martín et al., 1994) (Rubiaceae) as (*E*)-*O*-(6′)-cinnamoyl-4″-hydroxy-3″-methoxy-lyaloside (**3**). In a related plant, *Pauridiantha lyalii*, **3** was detected along with an analogous compound **5**, (*E*)-*O*-(6′)-cinnamoyl-4″-hydroxy-3″,5″-dimethoxy-lyaloside, as an inseparable mixture (Levesque, Jacquesi & Foucher, 1982). The present study is the first report concerning the alkaloidal content of *P. adusta*.

2. Results and discussion

The presence of a harmane moiety in compound **1** was demonstrated by the UV absorption maxima at 236, 291 and 351 nm and the occurrence of a conjugated ester band at 1670 cm^{-1} in the IR spectrum. To assist further structure elucidation, acetylation of **1** was performed, yielding the tetraacetylated compound **2**. Thus, derivative **2** showed similar UV and IR absorption bands with an additional IR band at 1720 cm^{-1}.

The ^{13}C NMR spectral data for **1** showed signals corresponding to 27 carbon atoms (Table 1), which is consistent with the biosynthetic pattern of indole alkaloids possessing a secologanin moiety as follows: 10 carbon atoms from tryptamine and 17 carbon atoms from secologanin including the glucose moiety. The ^{13}C NMR data of compound **2** showed four additional quaternary carbon atoms and four methyl carbon

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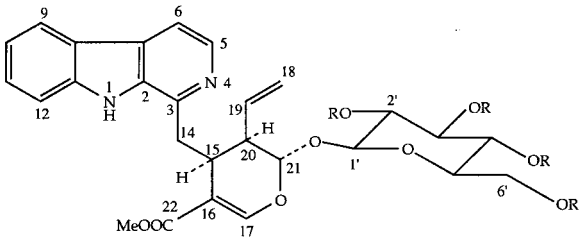
Table 1
^{13}C NMR spectral data for compounds **1**–**6** (75 MHz, d_6-DMSO, δ values)[a]

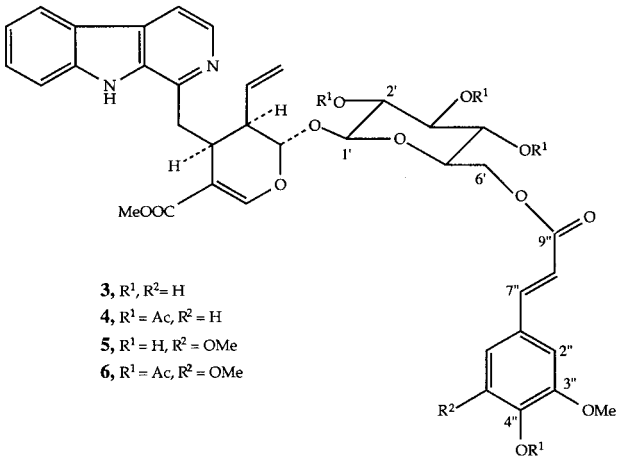
C	1	2	3	4	5	6
2	133.2 (s)	134.2 (s)	134.4 (s)	134.2 (s)	134.4 (s)	134.8 (s)
3	143.6 (s)	143.2 (s)	143.5 (s)	142.9 (s)	143.5 (s)	142.3 (s)
5	134.5 (d)	137.2 (d)	137.2 (d)	137.5 (d)	137.2 (d)	137.0 (d)
6	112.5 (d)	112.5 (d)	112.4 (d)	113.0 (d)	112.4 (d)	112.5 (d)
7	126.0 (s)	126.7 (s)	126.8 (s)	126.7 (s)	126.8 (s)	126.2 (s)
8	120.9 (s)	121.0 (s)	120.9 (s)	120.8 (s)	120.9 (s)	120.8 (s)
9	121.6 (d)	121.6 (d)	121.5 (d)	121.5 (d)	121.5 (d)	121.6 (d)
10	119.0 (d)	119.0 (d)	119.0 (d)	119.0 (d)	119.0 (d)	119.1 (d)
11	127.7 (d)	127.6 (d)	127.6 (d)	127.6 (d)	127.6 (d)	127.5 (d)
12	111.8 (d)	111.8 (d)	111.8 (d)	111.6 (d)	111.8 (d)	111.8 (d)
13	140.2 (s)	140.1 (s)	140.2 (s)	140.2 (s)	140.2 (s)	140.6 (s)
14	32.5 (t)	31.1 (t)	32.6 (t)	30.9 (t)	32.5 (t)	30.1 (t)
15	30.1 (d)	27.5 (d)	30.4 (d)	27.0 (d)	30.2 (d)	27.5 (d)
16	109.8 (s)	110.9 (s)	109.8 (s)	110.8 (s)	109.8 (s)	110.7 (s)
17	151.7 (d)	150.7 (d)	151.6 (d)	150.5 (d)	151.6 (d)	150.3 (d)
18	118.7 (t)	119.5 (t)	118.7 (t)	119.4 (t)	118.7 (t)	119.5 (t)
19	134.0 (d)	132.8 (d)	134.0 (d)	132.6 (d)	134.0 (d)	132.6 (d)
20	42.9 (d)	42.0 (d)	43.0 (d)	41.9 (d)	42.9 (d)	42.0 (d)
21	95.8 (d)	96.5 (d)	96.2 (d)	96.4 (d)	96.2 (d)	95.5 (d)
22	166.6 (s)	166.5 (s)	166.5 (s)	166.4 (s)	166.5 (s)	166.5 (s)
22-OMe	50.8 (q)	51.0 (q)	50.7 (q)	50.9 (q)	50.7 (q)	50.9 (q)
1′	98.7 (d)	95.5 (d)	99.2 (d)	95.5 (d)	99.1 (d)	96.4 (d)
2′	73.0 (d)	70.2 (d)	72.9 (d)	67.9 (d)	72.9 (d)	67.8 (d)
3′	77.3 (d)	71.6 (d)	76.5 (d)	71.6 (d)	76.5 (d)	71.6 (d)
4′	70.0 (d)	67.9 (d)	69.9 (d)	70.2 (d)	69.8 (d)	70.2 (d)
5′	76.8 (d)	70.9 (d)	74.0 (d)	70.9 (d)	74.0 (d)	70.9 (d)
6′	61.0 (t)	61.7 (t)	63.1 (t)	61.4 (t)	63.1 (t)	61.3 (t)
1″			125.4 (s)	132.8 (s)	124.2 (s)	132.1 (s)
2″			110.9 (d)	111.7 (d)	106.1 (d)	105.3 (d)
3″			147.7 (s)	151.0 (s)	147.8 (s)	151.9 (s)
4″			149.2 (s)	141.0 (s)	138.2 (s)	129.5 (s)
5″			115.2 (d)	123.0 (d)	147.2 (s)	151.8 (s)
6″			123.1 (d)	121.8 (d)	106.1 (d)	105.3 (d)
7″			114.2 (d)	117.6 (d)	114.6 (d)	117.8 (d)
8″			145.2 (d)	144.3 (d)	145.5 (d)	144.8 (d)
9″			166.6 (s)	165.8 (s)	166.5 (s)	166.3 (s)
3″-OMe			55.5 (q)	55.9 (q)	55.9 (q)	56.1 (q)
5″-OMe					55.9 (q)	56.1 (q)
Me*C*O		168.5 (s)		168.3 (s)		168.5 (s)
		169.1 (s)		168.5 (s)		169.0 (s)
		169.4 (s)		169.0 (s)		169.4 (s)
		169.9 (s)		169.4 (s)		167.7 (s)
*Me*CO		19.8 (q)		19.8 (q)		19.8 (q)
		20.3 (q)		20.2 (q)		20.0 (q)
		20.4 (q)		20.3 (q)		20.2 (q)
		20.5 (q)		20.3 (q)		20.3 (q)

[a] Multiplicities in parentheses assigned by DEPT.



1, R= H, lyaloside

2, R= Ac



3, R^1, R^2= H

4, R^1 = Ac, R^2 = H

5, R^1 = H, R^2 = OMe

6, R^1 = Ac, R^2 = OMe

atoms, indicating the presence of the acetylated hydroxy groups in the sugar moiety. The ESI-MS m/z of 527 $[M+1]^+$ was in accordance with the expected molecular weight for **1**, and correspondingly, the ESI-MS m/z of 695 $[M+1]^+$ for compound **2**, agreed with the tetraacetylated derivative proposed.

The ^{1}H NMR spectrum of **1** (Table 2) showed in the aromatic region two broad doublets at 8.17 and 7.55 ppm (H-9, H-12, J = 8 Hz) and two broad triplets (H-11, H-10, J = 8 Hz) at 7.50 and 7.21 ppm. A 2H AM system at 8.26 and 7.92 ppm (H-5, H-6, J = 5 Hz) was consistent with two protons in a pyridine-like skeleton. The chemical shifts and multiplicities observed, suggested the presence of a β-carboline. A HMBC experiment was conducted to assign the C-2, C-7, C-8 and C-13 signals, in which the exhibited long-range couplings of H-1 with the above mentioned quaternary carbon atoms were used as a starting point for the assignment. Correspondingly, H-5, H-6, H-9 and H-12 showed the expected long-range coupling correlations.

The presence in **1** of a doublet at down field 7.47 ppm (H-17, J = 1.5 Hz), suggested an olefinic proton of an α, β-unsaturated carbonyl system, which coupled with the multiplet at 3.71 ppm with an allylic coupling. The connection between H-17 with C-22 was confirmed by HMBC. A broad doublet at 5.37 ppm (H-21, J = 5 Hz) and a doublet at 4.56 ppm (H-1′, J = 8 Hz), together with the signals in the ^{13}C NMR spectrum at 95.8 and 98.7 ppm, evidenced the presence of two acetal groups in **1**. The signal at 5.37 ppm coupled with a multiplet at 2.73 ppm (H-20), which in turn is coupled with the H-19 at 5.66 ppm of a vinyl system. These observations are consistent with the presence of a secologanin moiety.

The DEPT-135 experiment demonstrated three

Table 2
^{1}H NMR spectral data for compounds **1**–**6** (600 MHz, d_6-DMSO, δ values, J in Hz)

H	1	2	3	4	5	6
1	11.40 (s)	11.40 (s)	11.30 (s)	11.38 (s)	11.28 (s)	11.40 (s)
5	8.26 (d, 5)	8.29 (d, 5)	8.22 (d, 5)	8.28 (d, 5)	8.22 (d, 5)	8.30 (d, 5)
6	7.92 (d, 5)	7.92 (d, 5)	7.87 (d, 5)	7.93 (d, 5)	7.86 (d, 5)	7.95 (d, 5)
9	8.17 (br d, 8)	8.17 (br d, 8)	8.15 (br d, 8)	8.18 (br d, 8)	8.14 (br d, 8)	8.19 (br d, 8)
10	7.21 (br t, 8)	7.20 (br t, 8)	7.20 (br t, 8)[a]	7.21 (br t, 8)	7.19 (br t, 8)	7.22 (br t, 8)
11	7.50 (br t, 8)	7.52 (m)[a]	7.48 (t, 8)	7.56 (m)[a]	7.50 (m)[a]	7.55 (m)[a]
12	7.55 (br d, 8)	7.52 (m)[a]	7.53 (m)	7.56 (m)[a]	7.50 (m)[a]	7.55 (m)[a]
14_a	3.13 (m)	3.02 (m)	3.11 (m)[a]	3.63 (m)[a]	3.24 (m)[a]	3.05 (m)
14_b	3.55 (m)	3.65 (m)	3.50 (m)[a]	3.64 (m)[a]	3.49 (m)	3.62 (m)[a]
15	3.71 (m)	3.65 (m)	3.64 (m)	3.65 (m)[a]	3.66 (m)	3.62 (m)[a]
17	7.47 (d, 1.5)	7.48 (d, 1.5)	7.45 (d, 1.5)	7.54 (d, 1.5)	7.45 (d, 1.5)	7.42 (d, 1.5)
18_a	4.75 (br d, 17)	4.51 (br d, 17)	4.77 (br d, 16)	4.51 (dd, 10,2)	4.72 (br d, 17)	4.53 (m)
18_b	4.94 (m)	4.84 (m)	4.91 (br d, 10)	4.85 (br d, 10)	4.89 (br d, 10)	4.86 (m)
19	5.66 (m)	5.54 (m)	5.65 (m)	5.55 (m)	5.64 (m)	5.56 (m)
20	2.73 (m)	2.86 (m)	2.71 (m)	2.86 (m)	2.72 (m)	2.85 (m)
21	5.37 (d, 5.0)	5.23 (d, 5.1)	5.44 (d, 5.2)	5.27 (d, 4.9)	5.42 (d, 5.3)	5.29 (d, 5.2)
OMe	3.28 (s)	3.55 (s)	3.28 (s)	3.54 (s)	3.32 (s)	3.53 (s)
1′	4.56 (d, 8)	5.19 (d, 8)	4.63 (d, 8)	5.22 (d, 8)	4.62 (d, 8)	5.23 (d, 8)
2′	3.02 (m)	4.84 (m)	3.23 (m)[a]	5.06 (t, 10)	3.10 (m)	5.06 (t, 10)
3′	3.18 (m)[a]	5.34 (t, 10)	3.23 (m)[a]	5.39 (m)	3.24 (m)[a]	5.39 (m)
4′	3.07 (m)	4.97 (t, 10)	3.11 (m)[a]	4.90 (m)	3.24 (m)[a]	4.90 (m)
5′	3.18 (m)[a]	4.09 (m)	3.50 (m)[a]	4.17 (m)	3.49 (m)	4.17 (m)
$6'_a$	3.45 (m)	4.03 (m)	4.29 (dd, 12,6)	4.21 (m)	4.31 (dd, 10,6)	4.20 (m)
$6'_b$	3.60 (m)	4.22 (dd, 12,4)	4.38 (dd, 12,2)	4.37 (dd, 12,4)	4.36 (dd, 10,4)	4.39 (m)
2″			7.20 (m)[a]	7.56 (m)[a]	6.92 (s)	7.15 (s)
5″			6.58 (d, 8)	7.06 (d, 8)		
6″			6.97 (br d, 8)	7.26 (br d, 8)	6.92 (s)	7.15 (s)
7″			6.46 (d, 16)	6.76 (d, 16)	6.52 (d, 16)	6.81 (d, 16)
8″			7.60 (d, 16)	7.63 (d, 16)	7.50 (m)[a]	7.62 (d, 16)
OMe			3.69 (s)	3.82 (s)	3.65 (s)	3.78 (s)
OMe					3.65 (s)	3.78 (s)
Me2′		1.89 (s)		1.90 (s)		1.90 (s)
Me3′		1.96 (s)		1.96 (s)		1.96 (s)
Me4′		1.98 (s)		2.01 (s)		2.01 (s)
Me6′		2.00 (s)				
Me4″				2.25 (s)		2.25 (s)
OH2′	5.08 (d, 5)		5.20 (d, 5)		5.19 (d, 5)	
OH3′	4.94 (m)		5.11 (d, 5)		5.11 (d, 5)	
OH4′	4.94 (m)		5.25 (d, 5)		5.25 (d, 5)	
OH6′	4.60 (m)					
OH4″			9.17 (s)		8.85 (s)	

[a] Overlapped signals. Chemical shifts were assigned based on HSQC experiments.

methylene groups in **1**. The signal at 118.7 ppm corresponded with the methylene carbon atom of the vinylic group (C-18). The methylene at 61.0 ppm was assigned to C-6′ of the sugar moiety. Finally the third methylene signal at 32.5 ppm was assigned to C-14. H-14_a and H-14_b (m, 3.13 and 3.55 ppm, respectively) exhibited a long-range coupling with C-2 and C-3, providing the evidence for a link between the harmane and the iridoidic system in **1**.

ESI-MS/MS of **1** showed an ion at m/z 365 $[M+1]^+$, indicating the loss of a neutral hexose moiety. HMBC experiments indicated that the sugar unit of **1** is bonded to C-21. As expected, the acetylated product **2** showed the corresponding signals from the sugar moiety shifted downfield. The doublet of the anomeric proton H-1′ moved from 4.56 to 5.19 ppm. The coupling constant of H-1′ ($J = 8$) indicated an axial proton and is consistent with the presence of a β-glucopyranoside skeleton in **1** and **2**. HMBC experiments conducted in **2** showed the long-range couplings of each of the methine protons of the pyranoside ring with the four carbonyl groups of the acetates. All signals were consistent with the published values of a β-D-glucopyranose (Bock, Rosendal Jensen & Juhl Nielsen, 1976).

Compound **3** was shown to be the ferulic acid derivative of **1**. Its identity was based on ESI-MS/MS analysis. The ESI-MS spectrum of **3** showed a molecu-

lar ion peak at m/z 703 $[M+1]^+$ and daughter ions at m/z 177 and m/z 365, which are consistent with a hydroxycinnamic derivative and the loss of a neutral sugar moiety. The UV spectrum of **3** displayed the characteristic absorption bands for the harmane skeleton at 238, 292 nm and an additional absorption at 330 nm due to the presence of a hydroxycinnamic fragment.

The ^{1}H NMR of **3** resembled the spectra obtained with **1**, but showed additional signals down field inferring the presence of a hydroxycinnamic ester. The signals for H-6$_a$′ and H-6$_b$′ were shifted down field from 3.45 and 3.60 ppm to 4.29 and 4.38 ppm, respectively, indicating the presence of an ester at C-6′. Additionally, a long-range coupling correlation was established between H-6$_a$′ and H-6$_b$′ with the carbonyl group of the hydroxycinnamate moiety, establishing the site of acylation at this position. The hydroxycinnamic derivative showed a 3H ABM system at 7.20, 6.97 and 6.58 ppm (H-2″, H-6″ and H-5″, respectively) and a 2H AM coupling system for H-7″, H-8″ at 7.60 and 6.46 ppm (J = 16 Hz), which also confirmed the presence of the (E) isomer of a ferulate residue.

Compound **5** was determined to be the sinapic acid derivative of **1**. The ESI-MS spectrum of **5** showed a molecular ion at m/z 733 $[M+1]^+$. This increment of 30 mass units compared with **3** suggested the presence of an additional methoxy group in **5**. Indeed, the daughter ion m/z 207 obtained in the ESI-MS/MS of **5**, suggested the presence of a sinapic acid derivative.

The ^{1}H NMR of **5** showed a different pattern for the hydroxycinnamic derivative. The ABM system in the aromatic region was replaced in **5** by an A_2 system, indicating a symmetric aromatic ring. Again, the coupling constant for H-7″ and H-8″ (J = 16 Hz) is consistent with the (E) isomer of the sinapic acid derivative **5**.

As expected, the acetylation of **3** and **5** afforded the tetraacetylated derivatives **4** and **6**. The spectroscopic data for **4** and **6** are presented in Tables 1 and 2.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR and 2D correlation spectra: Bruker AMX 600. HPLC/ESI/MS analyses were done with a Waters 626 LC System, Waters 996 photodiode array detector and Waters 600S Controller with a millenium chromatography manager 2010 v.2.15 and Rheodine rotary valve 7725i with a 20 μl loop. A Nucleosil 100-7C_{18} (200 × 4 mm i.d., 5 μm) analytical column was used and 20 μl samples were injected. The isocratic system consisted of 0.1 mM MeCN–HCO_2H–25% aq. NH_4OH (70:4:26). The flow was set to 1 ml/min. The frs. from HPLC were introduced directly to a triple stage quadrupole instrument (Finnigan TSD 700, San José, CA, USA). CD spectra were recorded using a JASCO J-715 spectropolarimeter; extrema are given between 350 and 230 nm.

3.2. Plant material

P. adusta Standley was collected in Reserva Nacional Biológica Tapantí in Cartago, Costa Rica in December 1995. The plant was identified by the Instituto Nacional de Biodiversidad (INBio) in Santo Domingo de Heredia, Costa Rica; a specimen voucher is maintained in its herbarium (Voucher No. J.F. Morales 5043).

3.3. Extraction and isolation

The leaves were freeze-dried, ground (0.56 kg) and extracted with EtOH (4 × 8 l) by stirring for 24 h each time at room temp. After concentration in vacuo, the extract (36.12 g) was acidified with 0.5 N aq. HCl and its neutral components were removed with Et_2O. After adjusting the pH to 8.15 extraction with chloroform (3×) and evpn of the solvent yielded 480 mg of the alkaloidal extract. CC on silica gel (0.063–0.200 mm, Merck) with $CHCl_3$–MeOH–25% aq. NH_4OH (84:14:1) was conducted in order to separate the two major frs. A (114 mg, R_f = 0.25) and B (78 mg, R_f = 0.16) which were active by UV and Schlittler reagent. Both frs. were submitted to HPLC/ESI/MS analysis. Fr. A consisted mainly of lyaloside (**1**, R_t = 6.22) and fr. B was composed of two sub-frs., namely B1 (**3**, R_t = 8.42) and B2 (**5**, R_t = 7.43). Purification by CC of fr. A gave an amorphous yellowish powder which was deduced to be **1** by comparison of the spectral data obtained with those reported in the literature (Levesque et al., 1975). Fr. B was further sepd with HPLC under the conditions mentioned above; 23 mg of **3** were obtained from B1 and 19 mg of **5** from B2. They were obtained as amorphous yellowish powders and were identified by comparing their spectroscopic data with those reported in the literature (Levesque et al., 1982).

Acetylation of **1**, **3** and **5**. An Ac_2O–Py (1:1) soln of **1** (15 mg), **3** (10 mg) and **5** (10 mg) each was stirred overnight and then evapd. The product was purified over silica gel by eluting with hexane–$CHCl_3$ (2:8) to give 10 mg of **2** as a colorless oil, 8 mg of **4** and 8 mg of **6**, both as pale yellow oils.

3.4. Lyaloside (*1*)

UV λ_{max}^{MeOH} nm (ε): 351 (4510), 291 (5660), 236 (12300), 215 (9425). CD (MeOH, c 0.010): $[\theta]_{350}$ −7282, $[\theta]_{290}$ −8158, $[\theta]_{286}$ −7181 sh, $[\theta]_{276}$ −6069,

$[\theta]_{254}$ −16443, $[\theta]_{234}$ 0, $[\theta]_{230}$ 4094. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1670. ^1H NMR: Table 2. ^{13}C NMR: Table 1. ESI-MS (MeOH + TFA 1%): 527 $[M+1]^+$, ESI-MS/MS at 527, *m/z* (rel. int.): 365 (60), 263 (100), 182 (30).

3.5. Tetra-(O-acetyl)-lyaloside (**2**)

UV λ_{max}^{MeOH} nm (ε) 290 (9321), 236 (23464), 206 (17857). CD (MeOH, *c* 0.06): $[\theta]_{350}$ −1490, $[\theta]_{348}$ −1519, $[\theta]_{300}$ −2532, $[\theta]_{290}$ −11266, $[\theta]_{286}$ −9367 sh, $[\theta]_{276}$ −8101, $[\theta]_{254}$ −31772, $[\theta]_{230}$ −5443. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1670. ^1H NMR: Table 2. ^{13}C NMR: Table 1. ESI-MS (MeOH + TFA 1%): 695 $[M+1]^+$, ESI-MS/MS at 695, *m/z* (rel. int.): 365 (60), 263 (100), 182 (30).

3.6. (E)-O-(6′)-Cinnamoyl-4″-hydroxy-3″-methoxy-lyaloside (**3**)

UV λ_{max}^{MeOH} nm (ε): 330 (10357), 292 (13257), 238 (26986). CD (MeOH, *c* 0.010): $[\theta]_{350}$ −1510, $[\theta]_{338}$ −4177, $[\theta]_{300}$ 0, $[\theta]_{290}$ −14810, $[\theta]_{286}$ −13702 sh, $[\theta]_{256}$ −59114, $[\theta]_{236}$ 0, $[\theta]_{233}$ 4462. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1640, 1600. ^1H NMR: Table 2. ^{13}C NMR: Table 1. ESI-MS (MeOH + TFA 1%): 703 $[M+1]^+$, ESI-MS/MS at 703, *m/z* (rel. int.): 365 (60), 263 (100), 177 (90), 182 (30).

3.7. (E)-Tetra-(O-acetyl)-O-(6′)-cinnamoyl-4″-hydroxy-3″-methoxy-lyaloside (**4**)

UV λ_{max}^{MeOH} nm (ε): 291 (53310), 238 (89379), 218 (69138). CD (MeOH, *c* 0.030): $[\theta]_{350}$ −3590, $[\theta]_{303}$ −2658, $[\theta]_{290}$ −18797, $[\theta]_{286}$ −13481 sh, $[\theta]_{276}$ −11582, $[\theta]_{254}$ −57531, $[\theta]_{230}$ −10253. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1680, 1640, 1600. ^1H NMR: Table 2. ^{13}C NMR: Table 1. ESI-MS (MeOH + TFA 1%): 871 $[M+1]^+$, ESI-MS/MS at 695, *m/z* (rel. int.): 365 (60), 263 (100), 219 (90), 182 (30).

3.8. (E)-O-(6′)-Cinnamoyl-4″-hydroxy-3″,5″-dimethoxy-lyaloside (**5**)

UV λ_{max}^{MeOH} nm (ε): 335 (27537), 292 (28676), 238 (76103), 206 (57353). CD (MeOH, *c* 0.020): $[\theta]_{350}$ 1510, $[\theta]_{338}$ −4177, $[\theta]_{319}$ 0, $[\theta]_{304}$ 833, $[\theta]_{297}$ 0, $[\theta]_{290}$ −14810, $[\theta]_{286}$ −13702 sh, $[\theta]_{256}$ −59113, $[\theta]_{250}$ −50474, $[\theta]_{246}$ −55348, $[\theta]_{233}$ 0, $[\theta]_{230}$ 4462. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1680, 1640, 1620. ^1H NMR: Table 2. ^{13}C NMR: Table 1. ESI-MS (MeOH + TFA 1%): 733 $[M+1]^+$, ESI-MS/MS at 733, *m/z* (rel. int.): 365 (60), 263 (100), 207 (50), 182 (30).

3.9. (E)-Tetra-(O-acetyl)-O(6′)-cinnamoyl-4″-hydroxy-3″,5″-dimethoxy-lyaloside(**6**)

UV λ_{max}^{MeOH}nm (ε): 292 (49500), 236 (88077), 207 (61538). CD (MeOH, *c* 0.060): $[\theta]_{350}$ −4525, $[\theta]_{317}$ 0, $[\theta]_{310}$ 881, $[\theta]_{302}$ 0, $[\theta]_{290}$ −21613, $[\theta]_{286}$ −15063 sh, $[\theta]_{254}$ −75158, $[\theta]_{230}$ −15348. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1680, 1640, 1600. ^1H NMR: Table 2. ^{13}C NMR: Table 1. ESI-MS (MeOH + TFA 1%): 901 $[M+1]^+$, ESI-MS/MS at 901, *m/z* (rel. int.): 365 (60), 263 (100), 249 (60), 182 (30).

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