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Glycosides from *Dicliptera riparia*

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Abstract

The dimeric monoterpenoid glycoside, diclipariside A, and two flavonoid glycosides, diclipariparisides B and C, together with six known compounds, β-sitosterol, 2,5-dimethoxy-*p*-benzoquinone, vanillic acid, daucosterol, lugrandoside and poliumonside, were isolated from the aqueous ethanol extract of the whole plants of *Dicliptera riparia* Nees. Their structures were determined based on analyses of spectroscopic data.

Keywords: *Dicliptera riparia* Nees; Acanthaceae; Diclipariside A; Diclipariside B; Diclipariside C

1. Introduction

Plants of the genus *Dicliptera* Juss (Acanthaceae) are distributed in tropical and sub-tropical regions (How et al., 1998), of which six species are found in the Yunnan Province, China (Wu et al., 1984). Due to their usage as a folk medicine, many phytochemical studies have been carried out on plants of this genus, and C_{15-31} fatty acids, flavonoids, carotenoids, α-amino acids, betulin, daucosterol and long-chain aliphatic hydrocarbons, have been isolated from *D. roxburghiana* and *D. chinensis* (Behuguna and Jangwan, 1986; Behuguna et al., 1987; Thapliyal et al., 1990; Giang and Pham, 1998). Among them hentriacontane and triacontane were confirmed to possess central nervous system depressive and muscular relaxation activities. In this investigation of *D. riparia*, a dimeric monoterpenoid glucoside, diclipariside A (**1**), and two flavonoid glycosides, diclipariparisides B (**2**) and diclipariparisides C (**3**), together with six known compounds, β-sitosterol (Kojima et al., 1990), 2, 5-dimethoxy-*p*-benzoquinone (Kardono et al., 1990), vanillic acid (Wang et al., 1991), daucosterol (Kojima et al., 1990), lugrandoside (Baudouin et al., 1988) and poliumonside (Andary et al., 1985), were isolated from the ethanolic extract of the whole plants of *D. riparia*. The three compounds **1–3** showed no cytotoxic activity in an vitro test.

2. Results and discussion

The aqueous ethanol extract of the whole plants of *D. riparia* was subjected repeatedly to column chromatography on silica gel to give diclipariparisides A (**1**), diclipariparisides B (**2**) and C (**3**), as well as β-sitosterol, 2,5-dimethoxy-*p*-benzoquinone, vanillic acid, daucosterol, lugrandoside and poliumonside.

Diclipariparisides A (**1**) was obtained as a yellowish powder, with 16 signals observed in its ^{13}C NMR spectrum. A conjugated carbonyl group was deduced from the IR peaks at 1700 and 1286 cm^{-1}, and the ^{13}C NMR (DEPT, Table 1) signal at δ 168.4 (*s*, C-1). A trisubstituted and a terminal double bond were deduced from ^{13}C NMR (DEPT) signals at δ 126.8 (*s*, C-2), 143.8 (*d*, C-3), 144.6 (*d*, C-7) and 114.5 (*t*, C-8). A monoterpene moiety **1A** was established on analysis of ^{1}H–^{1}H COSY, HMQC and HMBC spectra (Fig. 1 and Table 1). No NOESY correlation was observed between signals δ 6.75 (1H, *m*, H-3) and 1.77 (3H, *s*, H-9), indicating a double bond between C-2 and C-3 with an *E*-configuration (Table 1). Six additional signals at δ 96.1 (*d*), 71.4 (*d*), 72.0 (*d*), 68.7 (*d*), 71.8 (*d*) and 65.9 (*t*) indicated the presence of hexose in **1**, thus suggesting that compound

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Table 1
NMR spectral data of compound **1** in CD_3OD

No.	δ_H[a,b]	δ_C[b,c]	^1H–^1H COSY	HMBC	NOESY
1		168.4 (*s*)			
2		126.8 (*s*)			
3	6.75 (1H, *m*)	143.8 (*d*)	H-4, H-9	C-1	H-4
4	2.84 (1H, *ddd*, *J* = 10.8, 6.8, 3.2) 2.15 (1H, *ddd*, *J* = 10.8, 6.8, 3.2)	23.4 (*t*)	H-3, H-5	C-3, C-2	H-5, H-3
5	2.19 (1H, *ddd*, *J* = 13.2, 6.8, 3.2) 1.67 (1H, *ddd*, *J* = 13.2, 6.8, 3.2)	36.3 (*t*)	H-4	C-6	H-4, H-10
6		79.1 (*s*)			
7	6.04 (1H, *dd*, *J* = 17.8, 11.1)	144.6 (*d*)	H-8		H-8, H-1′
8	5.30 (1H, *dd*, *J* = 11.1, 1.6, H-8a), 5.25 (1H, *dd*, *J* = 17.8, 1.6, H-8b)	114.5 (*t*)	H-7	C-6	
9	1.77 (3H, *s*)	11.8 (*q*)	H-3	C-1, C-2, C-3	
10	1.32 (3H, *s*)	25.7 (*q*)		C-5, C-6, C-7	
1′	4.79 (1H, *d*, *J* = 8.0)	96.7 (*d*)	H-2′	C-6	H-7, H-2
2′	3.37 (1H, *dd*, *J* = 8.0, 6.0)	71.4 (*d*)	H-1′, H-3′	C-1′	
3′	4.09 (1H, *t*, *J* = 6.0)	72.0 (*d*)	H-2′, H-4′	C-1′	
4′	3.38 (1H, *m*)	68.7 (*d*)	H-3′, H-5′		
5′	3.86 (1H, *m*)	71.8 (*d*)	H-4′		
6′	4.35 (1H, *d*, *J* = 11.2) 3.94 (1H, *d*, *J* = 11.2)	65.9 (*t*)	H-5′		

[a] *J* in Hz.
[b] Signals were assigned by HMQC, HMBC and ^1H–^1H COSY experiments, δ in ppm.
[c] Multiplicity were determined by DEPT.

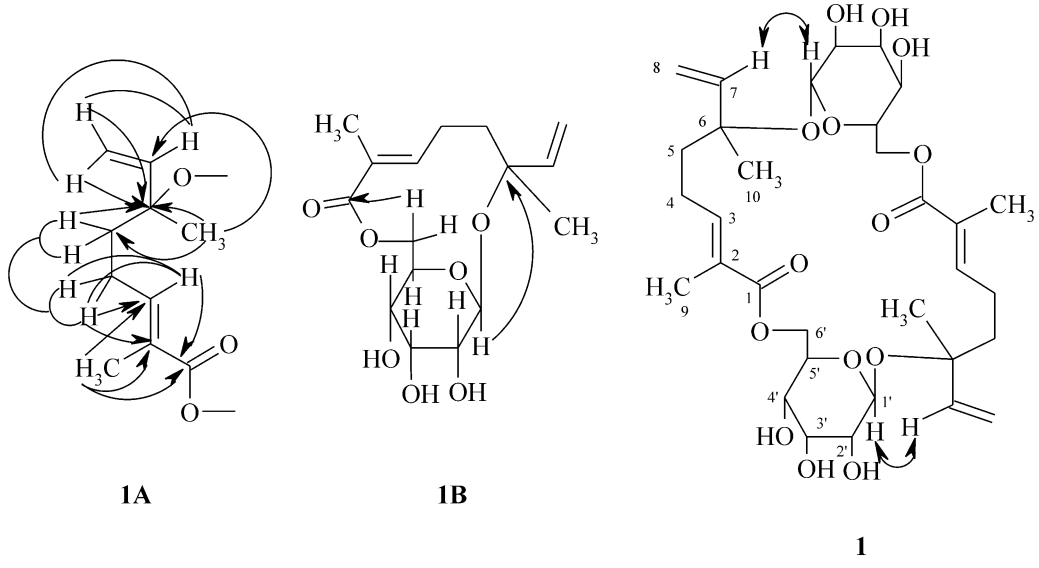

Fig. 1. Structure of compound **1** (→ key HMBC correlation,—key ^1H–^1H COSY correlation and ↔ Selected NOESY correlation).

1 is a glycoside of (2*E*)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid. HMBC correlations δ 4.35 (1H, *d*, *J* = 11.2 Hz, H-6′)/168.4 (*s*, C-1) and 4.79 (1H, *d*, *J* = 8.0 Hz, H-1′)/79.1 (*s*, C-6) suggested ester and ether bonds connecting **1A** and hexose. After hydrolyzing **1** in 1 M HCl (aq.), a compound with $[M\text{-}1]^-$ at *m*/*z* 345 in ESIMS (negative) was detected. This compound was further hydrolysed in alkali to give D-allose, and the ^1H NMR signal at δ 4.79 (1H, *d*, *J* = 8.0 Hz) of **1** suggested the presence of a β-D-allopyranosyl group. Thus, **1B** was elucidated as illustrated in Fig. 1.

However, the ion peak at *m*/*z* 655 ($[M\text{-}1]^-$) in the FABMS (negative), and the ion peaks at *m*/*z* 679 ($[M+Na]^+$) and 655 ($[M\text{-}1]^-$) by ESIMS in positive and negative modes, respectively, suggested the molecular weight of **1** should be 656. Tandem ESIMS (MS^2: 679 $[M+Na]^+ \rightarrow 351$ $[M/2+Na]^+$ in the positive mode, MS^2: 655→493 [M–allose-1]$^-$ and MS^3: 493→345 in the negative mode) confirmed this conclusion. The molecular formula $C_{32}H_{48}O_{14}$ of **1** was further established by the ion peak at *m*/*z* 657.3095 $[M+1]^+$ in its HRFABMS (positive). All MS data thus indicated that

1 could be a symmetric dimer, rather than **1B**, with each monomer having a molecular weight of 346. Therefore, compound **1** was elucidated as illustrated in Fig. 1. The configuration of C-6 could not be determined by the NOESY correlation observed between signals δ 6.04 (1H, *dd*, $J=17.8$, 11.1 Hz, H-7) and 4.79 (1H, *d*, $J=8.0$ Hz, H-1′) because of the free-rotation of single bonds. This compound should be a mesomeride with a symmetric axis C_2, for 16 signals in the ^{13}C NMR spectrum were observed, indicating that signals between two monoterpene moieties and between two allopyranosyl groups were equal. The ^1H NMR spectrum supported this conclusion, in which only signals for one monoterpene moiety were recognized. However, its measured optical rotation was not absolutely zero ($[\alpha]_D^{10}$ +0.127° (MeOH; *c* 0.11) with PE 241, $[\alpha]_D^{20}$ +0.217° (MeOH; *c* 0.06) with PE341).

Compound **2**, isolated as a yellow powder, gave an off-blue fluorescence when separated by TLC and examined under UV light (365 nm), which changed to a blue-green fluorescence followed by standing in NH_3 atmosphere for 5 s. The IR spectrum indicated a hydroxyl group by the absorbance at 3422 cm^{-1}, whereas a conjugated carbonyl could be deduced from the absorbance at 1657 cm^{-1}, and the ^{13}C NMR (Table 2) signal at δ 183.1 (*s*, C-4). The UV spectrum (λ_{max} at 275 and 327 nm) is typical for a flavone; the C-5 and C-3 positions are unsubstituted because no bathochromic shifts in the UV spectrum were observed when adding $AlCl_3$ and $AlCl_3$ + HCl to the methanolic solution of compound **2**. The ^1H NMR resonances at δ 7.35 (1H, *s*) and 6.91 (1H, *s*) could be assigned to H-5 and H-3 in view of the HMBC correlation of H-3 and H-5 with C-4 at δ 183.1 (*s*). The ^1H NMR signals at δ 8.03 and 7.23 (each 2 H, *d*, $J=9.2$ Hz, H-2′, 6′ and H-3′, 5′) indicated the presence of a 1,4-substituted phenyl ring (B ring). Two methoxyl groups resonated at δ 3.70 and 4.07 (each 3 H, *s*) in ^1H NMR spectrum, one of which could be assigned to 4′-OMe based on the HMBC cross signals between H-2′, H-3′ and 4′-OMe with C-4′ at δ 163.0. An acetyl group was deduced from the IR absorption at 1724 cm^{-1}, the ^1H NMR signal at δ 2.00 (3H, *s*, H-1‴) and the ^{13}C NMR (DEPT) resonance at δ 20.9 (*q*, C-1‴) and 170.6 (*s*, C-2‴), respectively (Fig. 2 and Table 2). The fragment ion peak at *m*/*z* 477 ([M-146–42 + H]$^+$) and 315 ([M-146–42–162 + H]$^+$) in the ESIMS (positive) suggested the presence of an acetyl and two hexose groups; however, only D-glucose was identified after acid hydrolysis of **2**. The acidic hydrolysate was then subjected to alkali hydrolysis, after which L-rhamnose was detected. Thus, L-rhamnose could be acetylated. The signals at δ 5.82 (1H, *d*, $J=6.8$, H-1″) and 5.46 (1H, *s*, H-1‴) showed the presence of β-D-glucose and α-L-rhamnose, respectively. C-4‴ should be acetylated in view of ^1H–^1H COSY correlations between H-6‴, H-5‴ and H-4‴, and the HMBC correlation at δ 5.69 (1H, *t*, $J=9.6$ Hz, H-4‴)/170.6 (*s*, C-2‴) and 1.26 (3H, *d*, $J=6.0$ Hz, H-6‴)/75.6 (*d*, C-4‴). A 1→6 linkage of rhamnose and glucose was concluded from the HMBC cross signal at δ 5.46 (1H, *s*, H-1‴)/67.3 (*t*, C-6″). C-1″ could be connected to C-6 considering the HMBC cross signals at δ 5.82 (1H, *d*, $J=6.8$, H-1″) and 7.35 (1H, *s*, H-5) with 157.6 (*s*, C-6), and the NOESY correlation at δ 5.82 (1H, *d*, $J=6.8$, H-1″)/7.35 (1H, *s*, H-5). Another methoxyl group should be located at C-7 according to the HMBC correlation between 7-OMe (4.07, 3H, *s*) and H-5 (7.35, 1H, s) with C-7 (134.0, *s*). Thus, **2** (dicliripariside B) could be 6,8-dihydroxy-

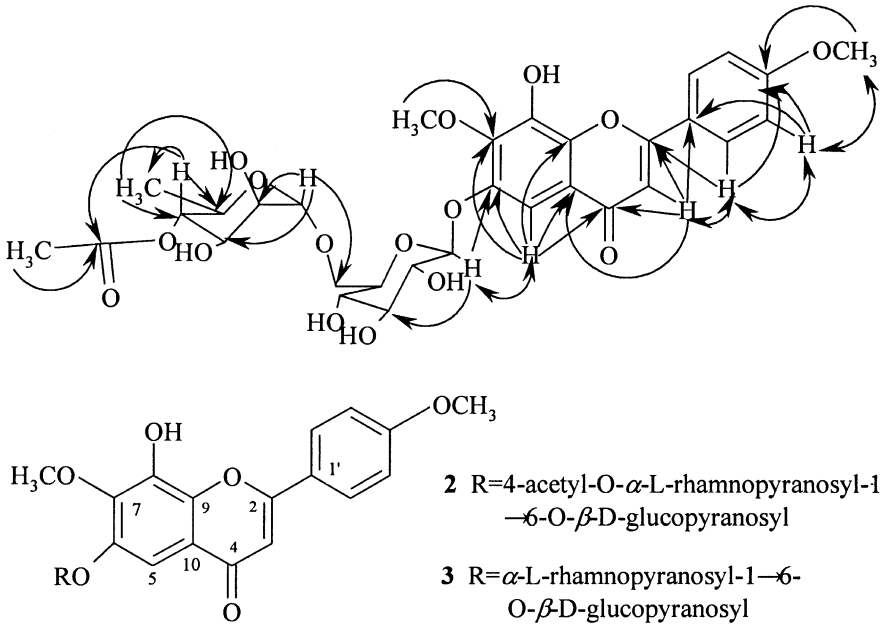

Fig. 2. Structures of compounds **2** and **3** (→ key HMBC correlation and ↔ selected NOESY correlation).

Table 2
NMR spectral data of compound **2** in pyridine-d_5

No.	δ_H[a,b]	δ_C[b,c]	^1H–^1H COSY	HMBC	NOESY
2		164.7 (*s*)			
3	6.91 (1H, *s*)	104.3 (*d*)		C-2, C-4, C-10, C-1′	H-2′
4		183.1 (*s*)			
5	7.35 (1H, *s*)	95.1 (*d*)		C-4, C-6, C-7, C-9, C-10	H-1″
6		157.6 (*s*)			
7		134.0 (*s*)			
8		153.1 (*s*)			
9		154.0 (*s*)			
10		107.1 (*s*)			
1′		122.9 (*s*)			
2′, 6′	8.03 (2H, *d*, *J* = 9.2)	128.7 (*d*)	H-3′, H-5′	C-2, C-4′	H-3, H-3′
3′, 5′	7.23 (2H, *d*, *J* = 9.2)	115.1 (*d*)	H-2′, H-6′	C-1′, C-4′	H-2′, 4′-OMe
4′		163.0 (*s*)			
1″	5.82 (1H, *d*, *J* = 6.8)	102.4 (*d*)	H-2″	C-7	H-5
2″	4.37 (1H, *m*)	74.6 (*d*)	H-1″, H-3″		
3″	4.19 (1H, *m*)	71.0 (*d*)	H-2″, H-4″		
4″	4.40 (1H, *m*)	78.3 (*d*)	H-3″, H-5″		
5″	4.33 (1H, *m*)	77.5 (*d*)	H-4″, H-6″		
6″	4.68 (1H, *d*, *J* = 10.8), 4.18 (1H, *d*, *J* = 10.8)	67.3 (*t*)	H-5″		
1‴	5.46 (1H, *s*)	102.0 (*d*)	H-2‴	C-6″, C-5‴, C-2‴, C-3‴	
2‴	4.63 (1H, *m*)	71.9 (*d*)	H-1‴, H-3‴		
3‴	4.55 (1H, *dd*, *J* = 9.6, 3.2)	70.2 (*d*)	H-2‴, H-4‴		
4‴	5.69 (1H, *t*, *J* = 9.6)	75.6 (*d*)	H-3‴, H-5‴	C-5‴, C-6‴, C-1⁗	
5‴	4.16 (1H, *m*)	67.0 (*d*)	H-4‴, H-6‴		
6‴	1.26 (3H, *d*, *J* = 6.0)	17.8 (*q*)	H-5‴	C-5‴, C-4‴	
7-OMe	4.07 (3H, *s*)	60.8 (*q*)		C-7	
4′-OMe	3.70 (3H, *s*)	55.4 (*q*)		C-4′	H-3′
1⁗		170.6 (*s*)			
2⁗	2.00 (3H, *s*)	20.9 (*q*)		C-1⁗	

[a] *J* in Hz.
[b] Signals were assigned by HMQC, HMBC and ^1H–^1H COSY experiments, δ in ppm.
[c] Multiplicity were determined by DEPT.

7,4′-dimethoxyflavone-6-*O*-(4-acetyl-α-L-rhamnopyranosyl)-1→6-*O*-β-D-glucopyranoside as shown in Fig. 2, which was proved further by the molecular formula $C_{31}H_{36}O_{16}$ (calc.: 664.2003) determined from the quasi-molecular ion peak at *m*/*z* 664.2002 in the HRFABMS (negative).

Compound **3**, a yellow powder, gave the same fluorescence behavior as that of **2**. The UV spectra in MeOH, MeOH + $AlCl_3$ and MeOH + $AlCl_3$ + HCl were very similar to those of **2**. The ^1H and ^{13}C NMR spectral data of compound **3** were also similar to that of **2**, except for signals of an acetyl group; the compound had a molecular formula of $C_{29}H_{34}O_{15}$ (calc.: 622.1898) as evidenced by the quasi-molecular ion peak at *m*/*z* 622.1953 in the HRFABMS (negative). The fragment ion peak at *m*/*z* 476 ([M-146]$^-$) and 313 ([M-146–162-H]$^-$) in the FABMS suggested the presence of two hexose groups and D-glucose and L-rhamnose were identified after acid hydrolysis of **3**. The signals at δ 5.82 (1 H, *d*, *J* = 6.8, H-1″) and 5.46 (1 H, *s*, H-1‴) showed the presence of β-D-glucose and α-L-rhamnose, respectively. Compound **3** was confirmed to be identical with the alkali hydrolysis product of **2** by co-TLC. Thus, the structure of **3** (dicliripariside C) was determined to be 6,8-dihydoxy-7,4′-dimethoxyflavone-6-*O*-(α-L-rhamnopyranosyl)-1→6-*O*-β-D-glucopyranoside as illustrated in Fig. 2.

3. Experimental

3.1. General

Mps were recorded on XRC-1 (uncorr.). Opitical rotations were measured with a Perkin-Elmer 241 automatic polarimeter. UV spectra were measured on a GBC Cintra 20 spectrometer and IR spectra were recorded on a Nicolet Protege 460 spectrometer. NMR spectra were obtained on an Avance 500 (500 MHz for ^1H and 125 MHz for ^{13}C, TMS as internal standard). CC was performed on silica gel of 200–300 mesh. MCI was purchased from Mitsubishi Chemical Company of Japan.

HRFABMS and FABMS were carried on a VG Auto-Spec-3000 (glycerol as matrix). TLC was carried out on silica gel (10–40 μm) precoated plates. Spots were visualized by spraying with 8% phosphomolybdic acid–EtOH solution followed by heating. Monosaccharides were identified by comparing with authentic monosaccharides on PC (the upper layer of *n*-BuOH:HOAc:H_2O = 4:1:5 as eluent) and TLC [the lower layer of $CHCl_3$:MeOH:H_2O, 15:6:2-HOAc (9:1) and EtOAC:pyridine:H_2O = 12:5:4 as eluent].

3.2. Plant material

Whole plants of *D. riparia* Nees were collected from Xishuangbanna, Yunnan Province, China, in September 1999, and identified by Professor J.Y. Cui (Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences). A voucher specimen (Z-15) is deposited at the Herbarium of Chengdu Institute of Biology, the Chinese Academy of Sciences.

3.3. Extraction and isolation

A sample of cut and dried whole plants (4.8 kg) was percolated with 92% EtOH (50 l×3) at room temp. After being concentrated in vacuo, ca. 330 g residue was obtained. The syrup was dissolved in 2.0 l of warm water (about 50 °C), cooled to room temp and successively extracted with petroleum ether (60–90 °C) (1.0 l×10), EtOAc (1.0 l×10) and *n*-BuOH (0.5 l×12), respectively.

The EtOAc extract (22.7 g) was dissolved in water (about 60 °C), cooled to room temp. and fractioned into four fractions FrB1–4 by CC packed with MCI gel eluted with a MeOH:H_2O gradient (from 50 to 100%). *β*-Sitosterol (12 mg) was obtained from FrB1 by CC repeatedly eluted with petroleum ether (60–90 °C):acetone (20:1). **1** (25 mg) was isolated from FrB4 by CC eluted with $CHCl_3$:MeOH (12:1). FrB2 was subjected to CC repeatedly eluted with petroleum ether (60–90 °C):acetone (4:1) to give 2,5-dimethoxy-*p*-benzoquinone (14 mg) and vanillic acid (14 mg). The *n*-BuOH extract (45.3 g) was dissolved in 1.0 l of warm water (about 50 °C) and absorbed by macroporous resin D101 with 100 Å of pore size and 400 m^2/g of specific surface area. The resin was eluted by water until no sugar was detected, then eluted by MeOH to yield 23 g fraction, which was divided into four fractions FrC1–4 by CC eluted with $CHCl_3$:MeOH:H_2O (4:1:0.1). Daucosterol (23 mg) was obtained from FrC1 by CC eluted with $CHCl_3$:MeOH (10:1). **2** (108 mg) was isolated from FrC3 by CC eluted with $CHCl_3$:MeOH:H_2O (4:1:0.1). Compound **3** (62 mg) was obtained from FrC2 by CC eluted with $CHCl_3$:MeOH:H_2O (6:1:0.1). FrC4 was firstly separated by CC with $CHCl_3$:MeOH:H_2O (3:1:0.1), then separated by CC packed with C-18 bonded silica gel with the elution of ethanol and water (1:4) to yield lugrandoside (280 mg) and poliumonside (65 mg).

The known compounds, *β*-sitosterol (Kojima et al., 1990), 2,5-dimethoxy-*p*-benzoquinone (Kardono et al., 1990), vanillic acid (Wang et al., 1991), daucosterol (Kojima et al., 1990), lugrandoside (Baudouin et al., 1988) and poliumonside (Andary et al., 1985) were identified by co-TLC with authentic samples and by comparison of their spectral data with those reported.

3.3.1. Diclipariside A (*1*)

Yellowish powder, mp 104–106 °C, $[\alpha]_D^{10}$ +0.127° (MeOH; *c* 0.11). IR ν_{max}^{KBr} cm^{-1}: 3448 (–OH), 2983, 2923, 1700 and 1286 (conjugated carbonyl), 1089, 1032 and 901. ^1H NMR and ^{13}C NMR spectral data: see Table 1. HRFABMS (+) *m/z*: 657.3095 (calc. for $C_{32}H_{48}O_{14}$: 656.3044). FABMS (−) *m/z* (rel. int.): 655 $[M-1]^-$ (100) and 345 (6). ESIMS (+) *m/z* (rel. int.): 679 $[M+Na]^+$ (100); MS^2: 679→351 $[M/2+Na]^+$ (100). ESIMS (−) *m/z* (rel. int.): 655 $[M-1]^-$ (100); MS^2: 655→493 [M-allose-1]$^-$ (100); MS^3: 493→345 (100).

Hydrolysis of dicliripariside A: Compound **1** (ca. 3 mg) was dissolved in 1 M HCl (aq.) and heated at 98 °C for 5 h. The mixture was then subjected to alkali hydrolysis in 1 M NaOH (aq.) under reflux for 3 h. Only D-allose was identified on PC and TLC with the authentic samples.

3.3.2. Dicliripariside B (*2*)

Yellow powder, mp 210–212 °C, $[\alpha]_D^{10}$ −0.9° (MeOH:pyridine (1:1); *c* 0.01). IR ν_{max}^{KBr} cm^{-1}: 3422 (–OH), 2924, 1724 (carbonyl of acetyl), 1657 (conjugated carbonyl), 1607 and 1570 (aromatic rings), 1462 and 1250. UV λ_{max}^{MeOH} nm (log *ε*): 275 (3.78) and 327 (3.88); UV $\lambda_{Max}^{MeOH+AlCl_3}$ nm (log *ε*): 280 (3.75) and 330 (3.82); UV $\lambda_{Max}^{MeOH+AlCl_3+HCl}$ nm: 279 (3.79) and 329 (3.88). ^1H NMR and ^{13}C NMR spectral data: see Table 2. HRFABMS (+) *m/z*: 664.2002 (calc. for $C_{31}H_{36}O_{16}$: 664.2003). FABMS (−) *m/z* (rel. int.): 664 $[M]^-$ (100) and 313 $[M–CH_3CO–Rha–Glc–1^-$ (95). ESIMS (+) *m/z* (rel. int.): 687 $[M+Na]^+$ (100), 477 $[M–CH_3CO–Rha+H]^+$ (10) and 315 $[M–CH_3CO–Rha–Glc+H]^+$ (100).

Hydrolysis of dicliripariside B: Compound **2** (ca. 6 mg) was dissolved in 3 M HCl (aq.) and heated at 90 °C for 2 h. D-Glucose was detected in the mixture by comparing with the authentic sample on PC and TLC. The mixture was then subjected to alkali hydrolysis in 1 M NaOH (aq.) under reflux for 3 h. D-Glucose and L-rhamnose were detected by PC and TLC with the authentic samples. Compound **2** (ca. 1 mg) was refluxed in 1 M NaOH (aq.) for 3 h. The mixture was extracted by EtOAc after adjusting pH = 6 by diluted HCl (aq.). The extract was confirmed to be identical to compound **7** on co-TLC.

*3.3.3. Diclipariside C (**3**)*

Yellowish powder, mp 238–240 °C, $[\alpha]_D^{10}$ −1.3° (MeOH:pyridine (1:1); *c* 0.016). IR $\nu_{max}^{KBr}cm^{-1}$: 3418 (–OH), 2933, 1656 (conjugated carbonyl), 1607 and 1570 (aromatic rings) and 1462. UV λ_{max}^{MeOH} nm (log ε): 277 (3.74) and 327 (3.83); UV $\lambda_{Max}^{MeOH+AlCl_3}$ nm (log ε): 280 (3.70) and 331 (3.81); UV $\lambda_{Max}^{MeOH+AlCl_3+HCl}$ nm (log ε): 280 (3.75) and 330 (3.85). ^{1}H NMR (pyridine-d_5): δ 8.06 (2H, *d*, *J* = 8.8 Hz, H-2′, 6′), 7.28 (2H, *d*, *J* = 8.8 Hz, H-3′, 5′), 7.34 (1H, *s*, H-5), 6.90 (1H, *s*, H-3), 5.79 (1H, *d*, *J* = 6.8 Hz, H-1″), 5.51 (1H, *s*, H-1‴), 4.07 (3H, *s*, 7-OMe), 3.73 (3H, *s*, 4′-OMe) and 1.57 (3H, *d*, *J* = 6.0 Hz, H-6‴). ^{13}C NMR (Pyridine-d_5): δ 164.7 (C-2), 104.3 (C-3), 183.1 (C-4), 95.1 (C-5), 157.7 (C-6), 134.0 (C-7), 153.1 (C-8), 154.0 (C-9), 107.1 (C-10), 122.9 (C-1′), 128.8 (C-2′, 6′), 115.1 (C-3′, 5′), 163.0 (C-4′), 102.5 (C-1″), 74.6 (C-2″), 71.2 (C-3″), 78.4 (C-4″), 77.6 (C-5″), 67.6 (C-6″), 102.3 (C-1‴), 72.0 (C-2‴), 69.8 (C-3‴), 74.0 (C-4‴), 72.8 (C-5‴), 18.5 (C-6‴), 60.8 (7-OMe) and 55.4 (4′-OMe). HRFABMS (+) *m*/*z*: 622.1953 (calc. for $C_{29}H_{34}O_{15}$: 622.1898). FABMS (−) *m*/*z* (rel. int.): 622 $[M]^-$ (80), 476 $[M\text{-}146]^-$ (5) and 313 $[M–Rha–Glc–H]^-$ (100).

Hydrolysis of dicliripariside C: Compound **3** (ca. 2 mg) was dissolved in 3 M HCl (aq.) and heated at 90 °C for 2 h. D-Glucose and L-rhamnose were detected by PC and TLC with the authentic samples from the reaction mixture.

References

Andary, C., Wylde, R., Heitz, A., Rascol, J.P., Roussel, J.L., Laffite, C., 1985. Poliumoside, a caffeic glycoside ester from *Teucrium belion*. Phytochemistry 24, 362–364.

Baudouin, G., Skaltsounis, A., Tillequin, F., Koch, M., 1988. Lutrandoside: a new phenylpropanoid glycoside from various *Digitalis* species. Planta Medica 48, 321–323.

Behuguna, R.P., Jangwan, J.S., 1986. Chemical investigations of *Dicliptera roxburghiana* Nees I. Herba Polonica 32, 71–73.

Behuguna, R.P., Jangwan, J.S., Kaiya, T., Sakakibara, J., 1987. Flavonoids and fatty acids of *Dicliptera roxburghiana*. International Journal of Crude Drug Research 25, 177–178.

Giang, T.S., Pham, H.T., 1998. Chemical components of *Dicliptera chinensis*. Tap Chi Duoc Hoc 1, 10–13.

How, F.C., Wu, T.L., Ko, W.C., Chen, T.C., 1998. A Dictionary of the Families and Genera of Chinese Seed Plants, second ed. South China Institute of Botany, Academic Sinica. Science Press, Beijing.

Kardono, L.B.S., Tsauri, S., Padmawinata, K., Pezzuto, J.M., Kinghorn, A.D., 1990. Cytotoxic constituents of the bark of *Plumeria rubra* colleted in Indonesia. Journal of Natural Products 53, 1447–1455.

Kojima, H., Sato, N., Hatano, A., Ogura, H., 1990. Sterol glucosides from *Prunella vulgaris*. Phytochemistry 29, 2351–2355.

Thapliyal, R.P., Jangwan, J.S., Behuguna, R.P., Prasad, C.R., 1990. Chemical investigation and pharmacological screening of *Dicliptera roxburghiana* Nees Part II. Himalayan Chemical and Pharmaceutical Bulletin 7, 17–28.

Wang, M.A., Zhang, H.D., Chen, Y.Z., 1991. Studies on chemical constituents of *Ajuga lupulina* Maxim. Journal of Lanzhou University (Natural Sciences) 27, 93–96.

Wu, C.Y., Yin, W.Q., Bao, S.Y., Tao, D.Y., Yuan, S.H., Deng, X.F., Yuan, S.X., You, H.Z., Lin, Q., 1984. Index Florae Yunnanensis, Tomus II, Institutum Botanicum Kunmingense Academiae Sinicae Edita. The People's Publishing House, Yunnan, China.