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SESQUITERPENE ALKALOIDS FROM *TRIPTERYGIUM HYPOGLAUCUM*

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Key Word Index—*Tripterygium hypoglaucum*; Celastraceae; root bark; sesquiterpenes; alkaloids; evonine; hyponine.

Abstract—Esters of three new (hyponines A–C) and four known sesquiterpene polyalcohol esters have been isolated from the root bark of *Tripterygium hypoglaucum*. The structures of the new compounds were elucidated at 7-(acetyloxy)-O^5-furanoyl-O^5-deacetyl-7-deoxo-evonine, 7-(acetyloxy)-O^{11}-furanoyl-O^{11}-deacetyl-7-deoxo-evonine and 7-(acetyloxy)-O^{11}-benzoyl-O^{11}-deacetyl-7-deoxo-evonine by spectroscopic means. This structural elucidation indicated that the structure of the known compound should be reversed.

INTRODUCTION

Species of the Celastraceae have been the subject of continued and growing interest, due to the range of biological activities exhibited [1–3], with some having been used in folk medicine [4] or as stimulants [5], from ancient times. In the last 20 years, many dihydroagarofuran sesquiterpenes have been isolated [3]. We have studied the sesquiterpene constituents of this genus and have described the isolation of triptofordins, triptofordinines, triptogelins and celafolins from *Tripterygium wilfordii* var. *regelii* [6] and *Celastrus stephanotifolius* [7]. Recently, we have found antitumour and antiviral activities from these sesquiterpenes [8–10]. In continuation of our previous interest in this area, three new alkaloids hyponines A (**1**), B (**2**) and C (**3**), and the known sesquiterpenes **4**–**7** have been isolated from the roots of *T. hypoglaucum*.

RESULTS AND DISCUSSION

Repeated column chromatography of the ethyl acetate-soluble fraction from the methanol extract of roots of *T. hypoglaucum*, yielded three new sesquiterpene pyridine alkaloids, hyponines A (**1**), B (**2**) and C (**3**), and four known compounds, **4**–**7**.

Hyponine A (**1**), an amorphous powder, showed ester carbonyl bands at 1757 and 1730 cm^{-1} in the IR spectrum, and the UV spectrum showed the presence of an aromatic moiety (222 and 249 nm). It contained five acetyl (Ac) groups (δ_H 1.85, 2.01, 2.16, 2.20 and 2.35), one furanoyl (Fu) group [δ_H 6.92 (*d*, J = 1.9 Hz), 7.46 (*s*), 8.37 (*d*, J = 1.9 Hz)], two tertiary methyl groups (δ_H 1.53 and 1.71), two sets of methylene protons [δ_H 3.63, 6.03 (each 1H, *d*, J = 11.7), 4.54, 5.14 (each 1H, *d*, J = 11.7 Hz)] and seven methine protons (δ_H 2.47, 4.72, 5.25, 5.39, 5.53, 5.56 and 7.13). It also contained one evonic acid moiety [2,3-substituted pyridine (δ_H 7.27, 8.04 and 8.70)], two secondary methyl groups (δ_H 1.19 and 1.42) and two methine protons (δ_H 2.56 and 4.63). The ^{13}C NMR spectrum of **1** indicated the presence of nine methyl carbons, two methylene carbons attached to an oxygen function, six methine carbons attached to an oxygen function, two methine carbons, eight ester carbonyl carbons, four quaternary carbons, one furanoyl group [δ_C 109.7 (*d*), 118.6 (*s*), 144.2 (*d*) and 149.6 (*d*)] and an evonic acid moiety [δ_C 9.5 (*q*), 11.8 (*q*), 36.4 (*d*), 44.9 (*d*), 121.1 (*s*), 125.2 (*s*), 137.5 (*d*), 151.5 (*d*), 165.0 (*s*), 169.1 (*s*, –COO–) and 173.9 (*s*, –COO–)]. These data agreed with a molecular formular of **1** as $C_{41}H_{47}O_{19}N$, which was supported by the HR mass spectral data. It was concluded that **1** is a sesquiterpene pyridine alkaloid derived from dihydroagarofuran polyol esters found in the Celastraceae [3]. The NMR spectra of **1** suggested that it was an evonine-type sesquiterpene alkaloid [11–16], having five acetyl groups and one furanoyl group. To confirm its structure, we recorded a 2D NMR. The ^1H-^1H COSY and the coupling among the six methine protons [δ_H 5.56 (1-H), 5.25 (2-H), 4.72 (3-H), 2.47 (6-H), 5.53 (7-H) and 5.39 (8-H)] revealed their connections in the dihydroagarofuran core; the remaining one methine at δ_H 7.13 (5-H) was correlated with the carbon signals at δ_C 50.3 (C-6), 73.9 (C-5)

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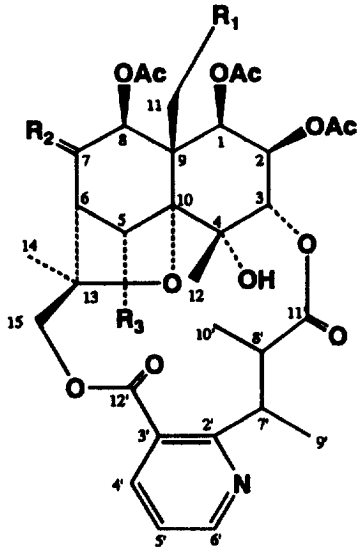
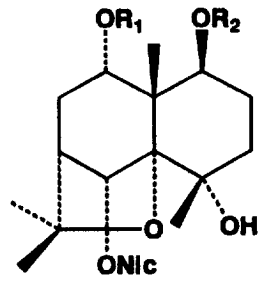


	R_1	R_2	R_3
1	OAc	β-OAc, α-H	OFu
2	OFu	β-OAc, α-H	OAc
3	OBz	β-OAc, α-H	OAc
4	OAc	β-OAc, α-H	OBz
5	OAc	O	OAc



	R_1	R_2
6	Bz	Bz
7	Bz	Ac
8	Ac	Bz

and 93.7 (C-10) in the HMBC spectrum. In the HMBC spectrum of **1**, the proton signal at δ_H 4.72 (3-H) was correlated with the carbon signals at δ_C 173.9 (C-11′); the proton signal at δ_H 2.56 (8′-H) with the carbon signals at δ_C 36.4 (C-7′) and 173.9 (C-11′); the proton signal at δ_H 8.04 (4′-H) with the carbon signal at δ_C 169.1 (C-12′); the proton signal at δ_H 6.03 (15-H″) with the carbon signals at δ_C 18.5 (C-14) and 169.1 (C-12′); these clearly indicated that the macrocycle structure was formed by ester linkages between one sesquiterpene molecule and evonic acid at positions 3 and 15.

In order to determine the position of the six ester groups (Ac × 5, Fu × 1) an HMBC spectrum was recorded. The proton signals assignable to acetyl methyl at δ_H 1.85, 2.01, 2.16, 2.20 and 2.35, were correlated with the carbon signals at δ_C 169.0, 168.8, 168.0, 170.2 and 170.1, respectively. The proton signals at δ_H 5.56 (1-H), 5.53 (7-H), 5.39 (8-H) and 4.54 (11-H) were correlated with the carbon signals at δ_C 169.0, 170.2, 168.8 and 170.1, respectively. These clearly indicated that the four acetyl ester groups could be placed on C-1, C-7, C-8 and C-11. The remaining ester groups are one furanoyl and one acetyl, and the ester linkage sites are C-2 and C-5. These ester linkage sites were determined as follows. The remaining ester carbonyl carbon signal in the ^{13}C NMR spectrum is a δ_C 161.8, which is assignable to the furanoyl ester carbon signal. In the HMBC spectrum, the proton signal at δ_H 7.13 (5-H) was correlated with a carbonyl carbon signal at δ_C 161.8; thus, the location of the furanoyl ester could be assigned to C-5. The relative stereochemistry of **1** was revealed by the coupling constants and NOESY spectrum; ^1H and ^{13}C NMR assignments were also revealed by 2D NMR spectra as shown in Tables 1 and 2. Therefore, the structure of hyponine A (**1**) was determined as 7-(acetyloxy)-O^5-furanoyl-O^5-deacetyl-7-deoxoevonine.

Hyponine B (**2**) was an amorphous solid which had a molecular formula $C_{41}H_{47}O_{19}N$. It was also a macrocylic sesquiterpene pyridine alkaloid and its nicotinate derivative unit in the macrocycle was evonic acid, the same as hyponine A. It contained five acetyl ester groups (δ_H 1.65, 1.80, 1.85, 2.05 and 2.18) and one furanoyl group (δ_H 6.94, 7.42 and 8.51), as revealed in the ^1H NMR spectrum. The molecular formular and the nature of the ester groups of compound **2** was the same as compound **1**; the ^{13}C NMR spectrum of compound **2** was very similar to that of compound **1** (Table 2). In the ^1H NMR spectra of both compounds, the chemical shifts and coupling patterns were almost the same except for 11-H_2 and 5-H (Table 1). This suggested that in **2** the ester linkage sites of **1** were exchanged at C-5 and C-11. To confirm the structure of **2**, we measured 2D NMR spectra. In the HMBC spectrum, the seven carbon signals were assigned as follows. The acetyl methyl proton signals at δ_H 1.65, 1.80, 1.85, 2.05 and 2.18, were correlated with the carbon signals at δ_C 170.0, 169.3, 169.0, 168.5 and 170.3, respectively; and the proton signals at δ_H 5.57 (1-H), 6.77 (5-H), 5.43 (7-H) and 5.26 (8-H) with the carbon signals at δ_C 169.3, 170.0, 170.3 and 169.0, respectively. The ester carbonyl carbon signal at δ_C 174.0 was correlated with the proton signals at δ_H 4.68 (3-H) and 2.50 (8′-H); and the carbon signal at δ_C 168.7 with the proton signals at δ_H 8.00 (4′-H) and

Table 1. ^{1}H NMR chemical shifts for compounds **1–4**

Proton	1	2	3	4
1-H	5.56 (*d*, 3.9)	5.57 (*d*, 3.7)	5.71 (*d*, 3.5)	5.52 (*d*, 3.8)
2-H	5.25 (*dd*, 2.4, 3.9)	5.19 (*dd*, 2.4, 3.7)	5.31 (*dd*, 2.4, 3.5)	5.20 (*dd*, 2.8, 3.8)
3-H	4.72 (*d*, 2.4)	4.68 (*d*, 2.4)	4.78 (*d*, 2.4)	4.64 (*br d*)
5-H	7.13 (*s*)	6.77 (*s*)	6.76 (*s*)	7.10 (*s*)
6-H	2.47 (*d*, 3.9)	2.31 (*d*, 3.8)	2.44 (*d*, 3.9)	2.44 (*d*, 3.8)
7-H	5.53 (*dd*, 3.9, 5.8)	5.43 (*dd*, 4.2, 5.8)	5.49 (*dd*, 3.5, 5.7)	5.47 (*dd*, 3.8, 5.9)
8-H	5.39 (*d*, 5.8)	5.26 (*d*, 5.8)	5.35 (*d*, 5.7)	5.33 (*d*, 5.9)
11-H′	4.54 (*d*, 13.7)	4.92 (*d*, 13.4)	5.10 (*d*, 13.3)	4.50 (*d*, 13.5)
11-H″	5.14 (*d*, 13.7)	5.02 (*d*, 13.4)	5.24 (*d*, 13.3)	5.10 (*d*, 13.5)
12-H_3	1.53 (*s*)	1.60 (*s*)	1.64 (*s*)	1.48 (*s*)
14-H_3	1.71 (*s*)	1.60 (*s*)	1.68 (*s*)	1.62 (*s*)
15-H′	3.63 (*d*, 11.7)	3.61 (*d*, 11.5)	3.70 (*d*, 11.4)	3.54 (*d*, 11.6)
15-H″	6.03 (*d*, 11.7)	5.92 (*d*, 11.5)	6.00 (*d*, 11.4)	5.95 (*d*, 11.6)
4′-H	8.04 (*dd*, 7.8, 1.9)	8.00 (*br d*, 7.7)	8.08 (*dd*, 7.8, 1.4)	7.97 (*dd*, 7.8, 1.4)
5′-H	7.27 (*dd*, 7.8, 4.9)	7.19 (*dd*, 7.7, 4.7)	7.27 (*dd*, 7.8, 4.7)	7.18 (*dd*, 7.8, 4.7)
6′-H	8.70 (*dd*, 4.9, 1.9)	8.63 (*br d*, 4.7)	8.71 (*dd*, 4.7, 1.4)	8.62 (*dd*, 4.7, 1.4)
7′-H	4.63 (*q*, 6.8)	4.60 (*q*, 6.9)	4.67 (*q*, 6.9)	4.64 (*q*, 7.1)
8′-H	2.56 (*q*, 6.8)	2.50 (*q*, 6.9)	2.61 (*q*, 6.9)	2.51 (*q*, 7.1)
9′-H_3	1.42 (*d*, 6.9)	1.33 (*d*, 7.0)	1.41 (*d*, 6.9)	1.36 (*d*, 6.9)
10-H_3	1.19 (*d*, 6.9)	1.13 (*d*, 7.0)	1.23 (*d*, 6.9)	1.12 (*d*, 6.9)
1-Ac	1.85 (*s*)	1.80 (*s*)	1.82 (*s*)	1.78 (*s*)
2-Ac	2.16 (*s*)	2.05 (*s*)	2.08 (*s*)	2.08 (*s*)
5-Ac	—	1.65 (*s*)	1.64 (*s*)	—
7-Ac	2.20 (*s*)	2.18 (*s*)	2.26 (*s*)	2.27 (*s*)
8-Ac	2.01 (*s*)	1.85 (*s*)	1.90 (*s*)	1.94 (*s*)
11-Ac	2.35 (*s*)	—	—	2.16 (*s*)

1: [5-Fu; 7.46 (*s*), 6.92 (*d*, 1.9), 8.37 (*br s*)]; **2**: [11-Fu; 7.42 (*s*), 6.94 (*br s*), 8.51 (*br s*)]. **3**: [11-Bz; (8.35 (*d*, 7.6), 7.51 (*dd*, 7.7, 7.6), 7.61 (*br d*, 7.5)]. **4**: [5-Bz; 8.24 (*d*, 7.5), 7.42 (*dd*, 7.5, 7.3), 7.50 (*br d*, 7.3)].

3.61, 5.92 (15-H_2). These data clearly indicated that the acetyl ester groups were located on C-1, C-5, C-7 and C-8 and that the macrocycle structure was formed at position 3 and 15. The only remaining ester carbonyl carbon is δ_C 162.2, which should be assignable to the furanoyl ester carbonyl carbon. In the HMBC spectrum of **2**, the proton signal at δ_H 5.02 (11-H) was correlated with the carbon signal at δ_C 162.2. Thus, the furanoyl ester group is at C-11. The remaining protons and carbons signals were assigned as shown in Tables 1 and 2 using 2D NMR including NOESY. Therefore, the structure of hyponine B (**2**) was determined to be 7-(acetyloxy)-O^{11}-furanoyl-O^{11}-deacetyl-7-deoxo-evonine.

Hyponine C (**3**), $C_{43}H_{49}O_{18}N$, contained five acetyl groups (δ_H 1.64, 1.82, 1.90, 2.08 and 2.26) and one benzoyl (Bz) group [δ_H 8.35 (2H, *d*, J = 7.6 Hz), 7.51 (2H, *dd*, J = 7.7, 7.6 Hz) and 7.61 (1H, *br d*, J = 7.6 Hz)], revealed by means of ^{1}H NMR. The ^{1}H and ^{13}C NMR spectra of **3** were very similar to those of compounds **1** and **2**, except for the ester moiety [**1** and **2**: Ac × 5, Fu × 1, **3**: Ac × 5, Bz × 1]. In the HMBC spectra of **3**, the carbonyl carbon signal at δ_C 166.0 was correlated with the proton signals at δ_H 5.10 (11-H) and 8.35 (benzoyl-*ortho*-H). This clearly indicated that the position of the benzoyl ester group in **3** is at C-11. The protons and carbons signals were assigned, as shown in Tables 1 and 2, in the same manner as described above. Thus, the structure of hyponine C (**3**) was formulated as shown.

Compounds **4–6** were identified from spectral comparison to be cangorinine E-I [17], evonine [16] and regelidine [18], respectively.

Compound **7**, $C_{31}H_{35}O_8N$, contained one acetyl, one benzoyl and one nicotinoyl group. The ^{13}C NMR spectral data (Table 3) were very similar to those of compound **6**, except for the signals due to the ester groups. The chemical shifts and coupling patterns of compound **6** and **7** were very similar, except for the proton signals assignable to 1-H (**6**, δ_H 5.61, **7**, δ_H 5.37). It was concluded that **7** is based on the same dihydroagarofuran skeleton of sesquiterpene polyol esters as compound **6**. In a comparison of the ^{1}H NMR spectrum of **7** with that of **6**, the 5-H and 8-H signals of both compounds resonated at almost the same chemical shifts, while the signal at δ_H 5.37 (1-H) of **7** resonated more upfield that of compound **6** (δ_H 5.61), indicating that the position of the acetyl ester was at C-1 in compound **7**. Compound **7** showed the same spectral data as 1-α-benzoyloxy-6β-nicotinoyloxy-9β-acetoxy-4β-hydroxy-dihydro-β-agarofuran (**8**) [19]. However, the structure was different to our estimated structure. To confirm our structure, we measured 2D NMR spectra. In the ^{1}H-^{1}H COSY and HMBC spectra, we confirmed the basic dihydroagarofuran skeleton and ester linkage sites. In the HMBC spectrum,

Table 2. ^{13}C NMR chemical shifts for compounds **1–4**

Carbon	1	2	3	4
1	73.2	73.1	73.2	73.2
2	68.7	68.7	69.0	68.7
3	75.7	75.6	75.6	75.8
4	70.6	70.6	70.7	70.6
5	73.9	74.2	74.2	74.8
6	50.3	50.5	50.4	50.4
7	68.9	68.8	69.0	69.1
8	70.6	70.2	70.6	70.8
9	52.1	52.7	52.6	52.2
10	93.7	94.0	94.0	93.7
11	60.0	60.0	61.0	60.0
12	22.9	23.8	24.1	22.9
13	84.1	84.3	84.4	84.2
14	18.5	18.6	18.6	18.4
15	69.8	69.8	69.9	69.9
2′	165.0	165.4	165.4	165.2
3′	125.2	125.0	125.0	125.1
4′	137.5	137.7	137.7	137.7
5′	121.1	121.1	121.1	121.1
6′	151.5	151.5	151.5	151.5
7′	36.4	36.3	36.4	36.3
8′	44.9	44.9	44.9	45.0
9′	11.8	11.8	11.9	11.8
10′	9.5	9.7	9.7	9.6
11′	173.9	174.0	174.0	173.9
12′	169.1	168.7	168.5	169.0
1-Ac	20.5	20.5	20.4	20.5
	169.0	169.3	169.5	169.1
2-Ac	21.0	21.1	21.1	21.1
	168.0	168.5	168.5	168.5
5-Ac	—	21.7	21.7	—
		170.0	169.7	
7-Ac	21.0	20.4	20.6	21.0
	170.2	170.3	170.0	170.2
8-Ac	20.4	20.3	20.2	20.4
	168.8	169.0	169.0	168.6
11-Ac	21.4	—	—	21.4
	170.1			170.2

1: (5-OCO-Fu; 161.8, 144.2, 118.6, 109.7, 149.6); **2**: (11-OCO-Fu; 162.2, 144.0, 119.2, 110.1, 149.3); **3**: (11-OCO-Bz; 166.0, 129.9, 133.5, 128.6, 130.2); **4**: (5-OCO-Bz; 165.8, 129.5, 130.3, 128.8, 133.6).

Table 3. ^{13}C NMR chemical shifts for compounds **6** and **7**

Carbon	6	7
1	73.3	72.6
2	38.9	38.8
3	23.5	23.4
4	70.8	70.8
5	80.9	80.9
6	49.1	49.0
7	31.9	31.9
8	73.3	72.8
9	51.8	51.5
10	91.6	91.5
11	20.1	19.7
12	24.0	24.0
13	84.5	84.5
14	25.9	25.8
15	29.7	29.8

the carbon signal at δ_C 169.9 was correlated with the proton signals at δ_H 1.56 (Ac) and 5.30 (1-H), the carbon signal at δ_C 164.9 with the proton signals at δ_H 8.43 (Nic-H) and 5.68 (5-H), and the carbon signal at δ_C 165.5 with the proton signals at δ_H 8.06 (Bz-H) and 5.10 (8-H). These observations clearly indicated that the ester linkage sites of acetyl, nicotinoyl and benzoyl are at C-1, C-5 and C-8, respectively. Thus, we propose the new structure **7** for compound **8**. In the structural elucidation of dihydroagarofuran sesquiterpenes, the determination of the linkage sites of ester groups containing more than three kinds of acids necessitates the use of X-ray crystallographic methods, comparison of chemical shifts, selective hydrolyses or HMBC spectra. By comparison of chemical shifts of similar compounds, it is difficult to determine the exact position of each ester, although this method does determine the difference between one or two esters in similar compounds. In some cases, using selective hydrolysis, it is also difficult to determine the exact position of each ester due to possible transesterification reactions during hydrolysis. We have used 2D NMR spectroscopy, including HMBC, to solve this problem. In the case of compound **8**, formerly elucidated by Gonzales *et al.* [19], the structure determined only using chemical shift comparisons was incorrect [7].

EXPERIMENTAL

^1H NMR: 400 MHz with TMS as int. standard. ^{13}C NMR: 100 MHz. CC: silica gel (Merck) and Sephadex LH 20 (Pharmacia). HPLC: GPC (Shodex packed column, GS-310), ODS (YMC packed column SH-345-5, S-5).

Plant material. Root outer bark of *T. hypoglaucum* (Levl.) Hutch was purchased in 1995 from Kumming of Yunnan Province in China.

Extraction and isolation. Root outer bark (15.3 kg) was crushed and extracted ×3 with MeOH (50 l) at 60° for 6 hr. The MeOH extracts were concd *in vacuo* to give a residue (860 g), which was partitioned between EtOAc and H_2O. The EtOAc layer was concd. to give a residue (314 g), which was chromatographed on a silica gel (1.6 kg) column. The column was eluted with solvents of increasing polarity [hexane–EtOAc (3:1, 3:2, 1:1, 1:2 and 1:4), EtOAc, EtOAc–MeOH (19:1, 9:1 and 4:1) and MeOH] to give 22 frs. Fr. 13 (12.8 g) was chromatographed on silica gel with CH_2Cl_2–MeOH (19:1 and 9:1) and MeOH to give 18 frs (frs 13.1–13.18). Fr. 13.2 (1.1 g) was chromatographed on Sephadex LH 20 with MeOH to give 7 frs (frs 13.2.1–13.2.8). Fr. 13.2.3 (0.6 g) was chromatographed using HPLC (GPC, MeOH) go give 3 frs (frs 13.2.3.1–13.2.3.3). Fr. 13.2.3.1 was

sepd using HPLC (ODS, MeOH–H_2O 4:1) and recycling GPC to give 16 mg of **5**. Fr. 13.2.3.2 was sepd using HPLC (ODS, MeOH–H_2O, 4:1) and recycling GPC to give 21 mg of **2**, 7 mg of **3** and 27 mg of **4**. Fr. 13.2.3.2.4 was sepd using HPLC (ODS, MeOH–H_2O, 3:1) to give 20 mg of **1**. Fr. 13.4 (0.3 g) was sepd using HPLC (GPC, MeOH) to give 4 frs (frs 13.4.1–13.4.4). Fr. 13.4.3. (112 mg) was sepd using HPLC (ODS, MeOH–H_2O, 4:1) to give 11 mg of **6** and 15 mg of **7**.

Hyponine A (**1**). Amorphous powder. $[\alpha]_D^{25}$ −27.5° ($CHCl_3$ *c* 0.7). IR ν_{max}^{KBr} cm^{-1}: 3503, 1757, 1730, 1639, 1372, 1239, 1162, 786, 760. UV λ_{max}^{MeOH} nm (ε): 222 (10000), 253 (5000), ^1H NMR: δ ($CDCl_3$): Table 1. ^{13}C NMR ($CDCl_3$): Table 2. FAB-MS *m/z*: 858 $[M+H]^+$. EI-MS *m/z* (rel. int.): 857 $[M]^+$ (100), 814 $[M-CH_3CO]^+$ (9), 798 (9), 738 (7), 624 (13), 262 (5), 206 (60), 178 (23), 161 (16), 150 (10), 134 (11), 107 (34), 95 (35), 43 (29). FAB HR-MS *m/z* 858.2820 $[M+H]^+$, $C_{41}H_{48}O_{19}N$ requires 858.2821.

Hyponine B (**2**). Amorphous powder. α_D^{25} −19.5° ($CHCl_3$ *c* 1.0). IR ν_{max}^{KBr} cm^{-1}: 3490, 1757, 1730, 1640, 1371, 1240, 785, 762. UV λ_{max}^{MeOH} nm (ε): 222 (8800), 249 (4000). ^1H NMR: δ ($CDCl_3$): Table 1. ^{13}C NMR ($CDCl_3$): Table 2. FAB-MS *m/z*: 858 $[M+H]^+$. EI-MS *m/z* (rel. int.): 857 $[M]^+$ (25), 814 $[M-CH_3CO]^+$ (4), 798 (6), 763 (20), 738 (5), 644 (6), 624 (5), 262 (9), 220 (12), 206 (100), 178 (28), 160 (21), 150 (14), 134 (15), 107 (60). FAB HR-MS *m/z* 858.2806 $[M+H]^+$, $C_{41}H_{48}O_{19}N$ requires 858.2821.

Hyponine C (**3**). Amorphous powder. α_D^{25} −15.5° ($CHCl_3$ *c* 0.8). IR ν_{max}^{KBr} cm^{-1}: 3490, 1752, 1725, 1371, 1235, 755, 716. UV λ_{max}^{MeOH} nm (ε): 228 (15000), 265 (3600). ^1H NMR: δ ($CDCl_3$): Table 1. ^{13}C NMR ($CDCl_3$): Table 2. FAB-MS *m/z*: 868 $[M+H]^+$. EI-MS *m/z* (rel. int.): 867 $[M]^+$ (59), 824 $[M-CH_3CO]^+$ (6), 808 (9), 764 (5), 748 (6), 634 (6), 262 (6), 220 (10), 206 (60), 178 (25), 161 (18), 134 (13), 105 (100), 43 (51). FAB HR-MS *m/z* 868.3018 $[M+H]^+$, $C_{43}H_{50}O_{18}N$ requires 868.3028.

Compound **5** (*evonine*). Amorphous powder. ^{13}C NMR ($CDCl_3$): δ 71.7 (*d*, C-1), 68.5 (*d*, C-2), 74.9 (*d*, C-3), 70.7 (*s*, C-4), 73.6 (*d*, C-5), 61.8 (*d*, C-6), 196.1 (*s*, C-7), 78.4 (*d*, C-8), 52.4 (*s*, C-9), 95.4 (*s*, C-10), 60.3 (*t*, C-11), 23.9 (*q*, C-12), 85.8 (*s*, C-13), 19.6 (*q*, C-14), 70.1 (*t*, C-15), 165.6 (*s*, C-2′), 124.5 (*s*, C-3′), 137.8 (*d*, C-4′), 121.2 (*d*, C-5′), 151.7 (*d*, C-6′), 36.3 (*d*, C-7′), 44.9 (*d*, C-8′), 11.9 (*q*, C-9′), 9.9 (*q*, C-10′), 173.9 (*s*, C-11′), 168.5 (*s*, C-12′), 1-Ac: 20.5 (*q*), 169.2 (*s*), 2-Ac: 21.0 (*q*), 168.5 (*s*), 5-Ac: 21.4 (*q*), 169.6 (*s*), 8-Ac: 20.1 (*q*), 169.1 (*s*), 11-Ac: 21.1 (*q*), 168.4 (*s*). FAB-HRMS *m/z* 762.2617 $[M+H]^+$, $C_{36}H_{43}O_{17}N$ requires 762.2609.

Compound **7**. IR ν_{max}^{KBr} cm^{-1}: 3497, 2951, 1722, 1592, 1367, 1284, 1113, 1027, 973, 716, ^1H NMR ($CDCl_3$): δ 1.35 (3H, *s*, 12-H_3), 1.42 (3H, *s*, 11-H_3), 1.51 (3H, *s*, 14-H_3), 1.52 (3H, *s*, 15-H_3), 1.56 (3H, *s*, 1-Ac), 2.26 (1H, *dd*, *J* = 16.3, 2.6 Hz, 7-H), 2.36 (1H, *br*, *s*, 6-H), 2.57 (1H, *ddd*, *J* = 16.3, 6.9, 3.3 Hz), 5.10 (1H, *br d*, *J* = 6.9 Hz, 8-H), 5.37 (1H, *dd*, *J* = 12.0, 4.0 Hz, 1-H), 5.68 (1H, *s*, 5-H), 7.40 (1H, *dd*, *J* = 8.0, 3.9, Nic-H), 7.44 (3H, *m*, Bz-H), 7.56 (1H, *t*, *J* = 7.4 Hz, Bz-H), 8.06 (2H, *d*, *J* = 7.5 Hz, Bz-H), 8.43 (1H, *d*, *J* = 8.0 Hz, Nic-H), 8.79 (1H, *br d*, *J* = 3.9 Hz, Nic-H), 9.37 (1H, *s*, Nic-H). ^{13}C NMR ($CDCl_3$): Table 3. EI-MS *m/z* (rel. int.): 537 $[M]^+$ (29), 522 (4), 451 (15), 432 (8), 400 (7), 372 (5), 295 (11), 181 (12), 124 (22), 105 (100), 43 (44). HR-MS *m/z* 537.2391 $[M]^+$, $C_{30}H_{35}O_8N$ requires 537.2363.

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