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STRUCTURES OF SESQUITERPENE POLYOL ALKALOIDS FROM *TRIPTERYGIUM HYPOGLAUCUM*

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Key Word Index—*Tripterygium hypoglaucum*; Celastraceae; root bark; sesquiterpene; pyridine alkaloid; hypoglaunine.

Abstract—Esters of four new (hypoglaunine A, B, C and D) and five known sesquiterpene polyalcohol esters have been isolated from the root barks of *Tripterygium hypoglaucum*. The structures of the new compounds were elucidated at 1,2,5,7,8-pentaacetoxy-11-furanoyl-4-hydroxy-3,15[2′-hydroxy-2′,3′-dimethyl-3′(3″-carboxy-4″-pyridyl)-propanoic acid]dicarbolactone-dihydroagarofuran, 1,5,7,8,11-pentaacetoxy-2-furanoyl-4-hydroxy-3,15[2′-hydroxy-2′,3′-dimethyl-3′(3″-carboxy-4″-pyridyl)-propanoic acid]dicarbolactone-dihydroagarofuran, 1,5,7,8,11-pentaacetoxy-2-benzoyl-4-hydroxy-3,15[2′-hydroxy-2′,3′-dimethyl-3′(3″-carboxy-4″-pyridyl)-propanoic acid]dicarbolactone-dihydroagarofuran and 1,2,5,7,8-pentaacetoxy-11-furanoyl-4-hydroxy-3,15[2′,3′-dimethyl-3′(3″-carboxy-4″-pyridyl)-propanoic acid]dicarbolactone-dihydroagarofuran by spectroscopic means.

INTRODUCTION

The genus of *Tripterygium* have been used as traditional Chinese drugs for the treatment of cancer and as an insecticide for hundreds of years. Recently, *T. wilfordii* Hook has been used to treat rheumatoid arthritis and ankylosing spondylitis in some Chinese clinics [1]. A number of sesquiterpene alkaloids have already been isolated from *T. wilfordii* and related species [2–13]. We have studied the sesquiterpene constituents of this genus and have described the isolation of hyponine A, B and C from the root barks of *T. hypoglaucum* [14]. In a continuation of our work on the chemical components of this plant, four new sesquiterpene pyridine alkaloids named hypoglaunine A (**1**), B (**2**), C (**3**) and D (**4**), along with five known sesquiterpene alkaloids, wilforine (**5**), wilforgine (**6**), wilfordine (**7**), wilfortrine (**8**) and euonymine (**9**) were isolated from the ethylacetate soluble fraction from the methanol extract of root barks of *T. hypoglaucum*.

About fifty macrocycle sesquierpene pyridine alkaloids have been isolated from the Celastraceae plants. These compounds may be roughly divided into two types, the evoninate type containing evonic acid and the wilfordate type containing wilforic acid in the macrocycle moiety. Also isomeric evoninate type [15] and isowilfordate type [8] compounds have been reported. In this paper, we report 8′-hydroxy compounds (**1**, **2** and **3**) which have the isomeric evoninate moiety and they are the first found in a natural source.

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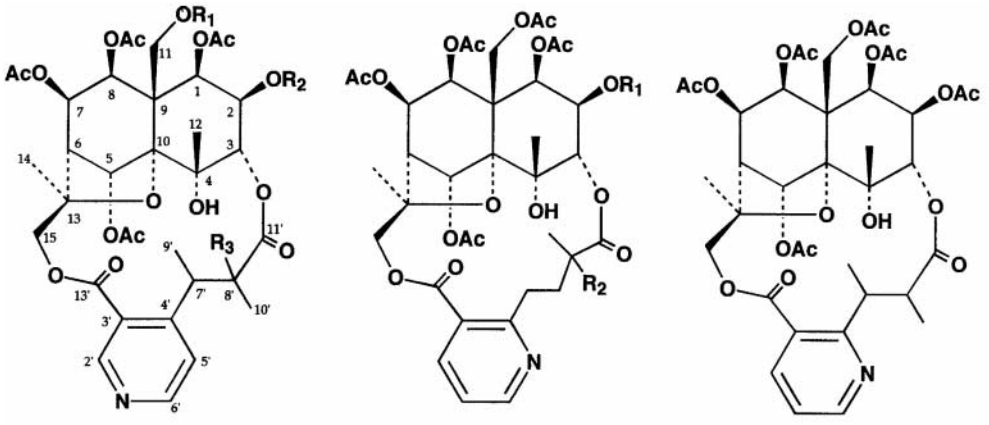
RESULTS AND DISCUSSION

Repeated column chromatography of the ethylacetate soluble fraction from the methanol extract of root barks of *Tripterygium hypoglaucum* (Levi.) Hutch yielded four new sesquiterpene pyridine alkaloids hypoglaunine A (**1**), B (**2**), C (**3**), D (**4**) and five known compounds **5**–**9**.

Hypoglaunine A (**1**) was obtained as an amorphous powder with the molecular formula $C_{41}H_{47}O_{20}N$. It showed ester carbonyl bands at 1747 and 1594 cm^{-1} in the IR spectrum and the UV spectrum showed the presence of an aromatic moiety (256 nm). It contained five acetyl (Ac) groups (δ_H 1.77, 1.90, 1.92, 2.15 and 2.25), one furanoyl (Fu) group [δ_H 7.00 (*d*, J = 2.0 Hz), 7.51 (*d*, J = 2.0 Hz), 8.54 (*s*)], three tertiary methyl groups (δ_H 1.36, 1.61 and 1.66), two sets of methylene protons [δ_H 4.24, 5.20 (each 1H, *d*, J = 11.2 Hz), 5.02, 5.05 (each 1H, *ABq*, J = 13.4 Hz)], seven methine protons (δ_H 2.47, 4.73, 5.10, 5.33, 5.37, 5.67, 6.84),



	R_1	R_2	R_3
1	Fu	Ac	OH
2	Ac	Fu	OH
3	Ac	Bz	OH
4	Fu	Ac	H

	R_1	R_2
5	Bz	H
6	Fu	H
7	Bz	OH
8	Fu	OH

9

one pyridyl moiety [δ_H 7.82 (*d*, J = 5.4 Hz), 8.69 (*d*, J = 5.4 Hz), 8.98 (*s*)], one secondary methyl group and one methine protons [δ_H 4.23 (*q*, J = 7.3 Hz)] in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum of **1** indicated that the presence of nine methyl carbons, two methylene carbons attached to oxygen functions, six methine carbons attached to oxygen functions, one methine carbon, eight ester carbons, five quaternary carbons, one furanoyl group and one pyridyl moiety [δ_C 123.6 (*d*), 127.9 (*s*), 151.4 (*d*), 151.9 (*s*), 152.6 (*d*)]. From these facts, compound **1** was assumed to be a sesquiterpene pyridine alkaloid derived from dihydroagarofuran polyol esters such as hyponine A, B and C [14]. To confirm the structure of hypoglaunine A (**1**), we measured the 2D NMR spectra. The ^{1}H–^{1}H COSY and the coupling among the six methine protons [δ_H 5.67 (1-H), 5.37 (2-H), 4.73 (3-H), 2.47 (6-H), 5.10 (7-H) and 5.33 (8-H)] revealed their connections in the dihydroagarofuran core, the remaining one methine at δ_H 6.84 (5-H) was correlated with the carbon signals at δ_C 51.0 (C-6), 53.4 (C-9), 93.6 (C-10) and 83.8 (C-13) in the HMBC spectrum. on the other hand, the proton signal [δ_H 8.98 (*s*, 2′-H)] was correlated with the carbon signals at δ_C 127.9 (C-3′), 167.7 (C-12′) and 152.6 (C-6′); the proton signal [δ_H 4.23 (7′-H)] was correlated with the carbon signals at δ_C 127.9 (C-3′), 123.6 (C-5′), 17.4 (C-9′), 77.1 (C-8′) and 175.2 (C-11′); the proton signal at δ_H 1.36 (10′-H3) with the carbon signals at δ_C 42.3 (C-7′), 77.1 (C-8′) and 175.2 (C-11′). These facts indicated that the pyridyl moiety was 2-hydroxy-2,3-dimethyl-3(3′-carboxy-4′-pyridyl)-propanoic acid.

In the HMBC spectrum of **1**, the proton signal at δ_H 4.73 (3-H) was correlated with the carbon signals at δ_C 175.2 (C-11′), the proton signal at δ_H 5.20 (15-H′) with the carbon signals at δ_C 18.7 (C-14) and 167.7 (C-12′), the proton signal at δ_H 8.98 (2′-H) with the carbon signal at δ_C 167.7 (C-12′). These facts indicated that the one macrocycle structure was formed by ester linkages between one sesquiterpene molecule and a pyridyl unit at position C-3 and C-15.

In order to determine the position of the six ester groups (Ac × 5, Fu × 1), an HMBC spectrum was recorded. The proton signals at δ_H 5.02, 5.05 (11-H′, H″), 7.00 (3″-H, furanoyl) were correlated with the carbon signal at δ_C 162.3, it clearly indicated that the furanoyl ester could be assigned to C-11. The proton signals assignable to acetyl methyl at δ_H 1.77, 1.90, 1.92, 2.15 and 2.25 were correlated with the carbon signals at δ_C 170.1, 169.3, 168.8, 168.4 and 169.6, respectively. The proton signals at δ_H 5.67 (1-H), 5.37 (2-H), 6.84 (5-H) and 5.33 (8-H) were correlated with the carbon signals at δ_C 169.6, 168.4, 170.1 and 168.8, respectively. These data indicated that the four acetyl ester groups could be located on C-1, C-2, C-5 and C-8. Except for the macrocycle ester linkage site at C-3 and C-15, the remaining ester linkage site at C-7 was bonded by the remaining acetyl group. The relative stereochemistry of **1** was revealed by the coupling constants and NOESY spectrum, ^{1}H and ^{13}C NMR assignments were confirmed by 2D NMR spectra as shown in Tables 1 and 2. Therefore, the structure of hypoglaunine A (**1**) was determined as shown.

Hypoglaunine B (**2**) was an amorphous solid which had a molecular formula $C_{41}H_{47}O_{20}N$. It was also a macrocyclic sesquiterpene pyridine alkaloid and its pyridyl derivative unit in the macrocycle was also a 3′,4′-substituted pyridyl type, the same as hypoglaunine A (**1**). It contained five acetyl ester groups [δ_H 1.85, 1.98, 2.18, 220 and 2.33], one fura-

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

Proton	**1**	**2**	**3**	**4**
1-H	5.67(*d*, 3.4)	5.68(*d*, 3.9)	5.73(*d*, 3.9)	5.63(*d*, 3.9)
2-H	5.37(*dd*, 2.9, 3.4)	5.54(*dd*, 2.4, 3.9)	5.64(*dd*, 2.4, 3.9)	5.26(*dd*, 2.4, 3.9)
3-H	4.73(*d*, 2.9)	4.79(*d*, 2.4)	4.84(*d*, 2.4)	4.75(*d*, 2.4)
5-H	6.84(*s*)	7.05(*s*)	7.05(*s*)	6.87(*s*)
6-H	2.47(*d*, 3.4)	2.42(*d*, 3.9)	2.44(*d*, 3.9)	2.40(*d*, 3.9)
7-H	5.10(*dd*, 3.4, 6.4)	5.53(*dd*, 3.9, 6.3)	5.54(*dd*, 3.9, 5.9)	5.51(*dd*, 3.9, 6.4)
8-H	5.33(*d*, 6.4)	5.39(*d*, 6.3)	5.40(*d*, 5.9)	5.35(*d*, 6.4)
11-H′	5.02(*d*, 13.4)	4.29(*d*, 13.6)	4.40(*d*, 13.7)	4.97(*d*, 13.2)
11-H″	5.05(*d*, 13.4)	5.48(*d*, 13.6)	5.47(*d*, 13.7)	5.11(*d*, 13.2)
12-H3	1.66(*s*)	1.56(*s*)	1.65(*s*)	1.71(*s*)
14-H3	1.61(*s*)	1.63(*s*)	1.64(*s*)	1.68(*s*)
15-H′	4.24(*d*, 11.2)	4.29(*d*, 11.7)	4.30(*d*, 11.7)	3.70(*d*, 11.7)
15-H″	5.20(*d*, 11.2)	5.14(*d*, 11.7)	5.15(*d*, 11.7)	6.08(*d*, 11.7)
2′-H	8.98(*s*)	9.00(*s*)	9.00(*s*)	8.99(*s*)
5′-H	7.82(*d*, 5.4)	7.83(*d*, 4.9)	7.85(*d*, 5.4)	7.37(*d*, 5.4)
6′-H	8.69(*d*, 5.4)	8.69(*d*, 4.9)	8.69(br *d*)	8.71(*d*, 5.4)
7′-H	4.23(*q*, 7.3)	4.24(*q*, 6.8)	4.26(*q*, 7.3)	4.72(*q*, 7.3)
8′-H	–	–	–	2.47(*q*, 6.8)
9′-H3	1.21(*d*, 7.3)	1.19(*d*, 6.8)	1.20(*d*, 7.3)	1.37(*d*, 7.3)
10′-H3	1.36(*s*)	1.38(*s*)	1.39(*s*)	1.09(*d*, 6.8)
1-Ac	2.25(*s*)	2.20(*s*)	1.84(*s*)	1.87(*s*)
2-Ac	2.15(*s*)	–	–	2.13(*s*)
5-Ac	1.77(*s*)	2.18(*s*)	2.21(*s*)	2.25(*s*)
7-Ac	1.90(*s*)	1.98(*s*)	2.18(*s*)	1.71(*s*)
8-Ac	1.92(*s*)	1.85(*s*)	1.96(*s*)	1.94(*s*)
11-Ac	–	2.33(*s*)	2.28(*s*)	–

1: [11-Fu: 7.51 (*d*, 2.0), 7.00 (*d*, 2.0), 8.54 (*s*)]; **2**: [2-Fu: 7.51(br *s*), 6.89 (br *s*), 8.32 (*s*)]; **3**: [2-Bz: 8.13(2H, *d*, 7.3), 7.52 (2H, *dd*, 7.3, 7.8), 7.65 (br t, 7.8)]; **4**: [11-Fu: 7.50 (br *s*), 7.03 (*d*, 1.0), 8.60 (*s*)].

noyl group [δ_H 6.89, 7.51 and 8.32] found in the ^{1}H NMR spectrum. The compound **2** had the same molecular formula and ester groups as that of compound **1**. The ^{13}C NMR spectral data was very similar to that of compound **1**. In the HMBC spectrum of **2**, the proton signals at δ_H 5.68 (1-H) and 2.20 (acetyl methyl) were correlated with the carbon signal at δ_C 169.5; δ_H 7.05 (5-H) and 2.18 (acetyl methyl) with the carbon signal at δ_C 169.8; δ_H 5.39 (8-H), 1.85 (acetyl methyl) with the carbon signal at δ_C 169.0; δ_H 5.48 (11-H″) and 2.33 (acetyl methyl) with the carbon signal at δ_C 170.6. The ester carbonyl carbon signal at δ_C 175.2 (C-11′) was correlated with the proton signal at δ_H 4.79 (3-H) and 1.38 (10′-H3) and the carbon signal at δ_C 167.7 (C-12′) was correlated with the proton signals at δ_H 9.00 (2′-H), 4.29 (15-H′) and 5.14 (15-H″). These facts clearly indicated that four acetyl groups were located on C-1, C-5, C-8, C-11 and the macrocycle structure was formed by ester bonds at positions C-3 and C-15. The remaining ester linkage sites were C-2 and C-7. However, the proton signals at δ_H 5.54, 5.53 (2-H and 7-H) were very similar and it was difficult to determine the position of the furanyl group at C-2 or C-7. To confirm the structure of compound **2**, we measured the ^{1}H NMR spectrum in the pyridine-d_5 which revealed the separate proton signals at δ_H 6.13 (2-H) and 5.95 (7-H). In its HMBC pyridine-d_5 spectrum, the proton signal at δ_H 6.13 (2-H) was correlated with the carbon signal at δ_C 162.0 which was assigned to the furanoyl group, to indicate that the furanoyl group was located on C-2 and the last acetyl group was assigned to C-7. The remaining proton and carbon signals were assigned as shown in Tables 1 and 2 by using 2D NMR and NOESY spectra. Therefore, the structure of hypoglaunine B (**2**) was determined as shown.

Hypoglaunine C (**3**), $C_{43}H_{49}O_{19}N$, contained five acetyl groups [δ_H 1.84, 1.96, 2.18, 2.21, 2.28] and one benzoyl (Bz) group [δ_H 8.13 (2H, *d*, J = 7.3 Hz), 7.52 (2H, *dd*, J = 7.3, 7.8 Hz), 7.65 (1H, *br t*, J = 7.8 Hz)] revealed by means ^{1}H NMR spectrum. The spectral data of compound **3** was very similar to that of compound **1** and **2** by comparison with their ^{1}H and ^{13}C NMR spectra, except for the ester moiety [**1** and **2**: Ac × 5, Fu × 1, **3**: Ac × 5, Bz ×1]. It is assumed that the different points on the structures of **1**, **2** and **3** were reduced to produce ester linkage sites. In the HMBC spectrum of **3**, the carbonyl carbon signal at δ_C 164.8 was correlated with the proton signals at δ_H 5.64 (2-H) and 8.13 (benzoyl-*ortho*-H). It clearly indicated that the benzoyl ester group of **3** was located on C-2. The proton and carbon signals were assigned as shown in Tables 1 and 2 in the same manner as described above. Therefore, the structure of hypoglaunine C (**3**) was determined as shown.

Hypoglaunine D (**4**), $C_{41}H_{47}O_{19}N$, contained five acetyl groups, [δ_H 1.71, 1.87, 1.94, 2.13 and 2.25] and one furanoyl group [δ_H 7.03 (*d*, 1.0), 7.50 (*br s*), 8.60 (*s*)] determined from the ^{1}H NMR spectrum. The ^{13}C NMR spectral data was very similar to that of compound **1** except for the carbon signals at position C-7′, C-8′, C-9′ and C-10′ (Table 2). It was assumed to be 8′-dehydroxy hypoglaunine A

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

Carbon	1	2	3	4
1	73.1	73.0	72.8	73.3
2	68.8	68.3	68.4	69.1
3	78.0	77.9	77.5	76.0
4	70.9	71.7	70.3	71.0
5	75.4	74.7	74.1	74.4
6	51.0	51.1	50.6	50.8
7	69.2	69.3	68.8	69.0
8	71.1	71.2	70.6	70.4
9	53.4	52.8	52.2	53.0
10	93.6	93.6	93.2	94.4
11	60.4	60.6	60.3	60.1
12	23.4	22.8	22.6	23.8
13	83.8	83.6	83.3	84.6
14	18.7	18.7	18.6	18.7
15	70.0	69.9	69.7	70.3
2′	151.4	151.7	151.3	151.0
3′	127.9	127.7	128.5	125.4
4′	151.9	152.0	151.8	156.6
5′	123.6	123.6	123.5	121.7
6′	152.6	152.7	152.5	153.0
7′	42.3	42.3	41.8	33.4
8′	77.1	77.1	77.2	45.8
9′	17.4	17.4	17.2	11.5
10′	24.3	24.2	24.0	10.0
11′	175.2	175.2	174.9	173.9
12′	167.7	167.7	167.6	168.1
1-Ac	21.5	21.5	20.4	20.7
	169.6	169.5	169.2	169.4
2-Ac	20.9	–	–	21.2
	168.4			168.8
5-Ac	20.3	20.9	21.6	21.8
	170.1	169.8	169.6	170.1
7-Ac	20.4	20.4	21.0	20.5
	169.3	168.8	170.0	170.4
8-Ac	20.2	20.3	20.5	20.5
	168.8	169.0	168.9	169.1
11-Ac	–	21.2	21.2	–
		170.6	170.4	

1: (11-OCO-Fu: 162.3, 144.1, 110.9, 119.6, 149.3); **2**: (2-OCO-Fu: 160.9, 144.4, 110.0, 118.5, 149.0); **3**: (2-OCO-Bz: 164.8, 128.5, 130.0, 128.8, 133.9); **4**: (11-OCO-Fu: 162.4, 144.1, 110.3, 119.4, 149.6).

(**1**). In the HMBC spectrum of **4**, the carbon signal at δ_C 162.4 was correlated with the proton signals at δ_H 4.97 (11-H′), 5.11 (11-H″) and 7.03 (furanoyl, 4″-H); the proton signals at δ_H 5.63 (1-H), 5.26 (2-H), 6.87 (5-H), 5.51 (7-H) and 5.35 (8-H) were correlated with the acetyl carbonyl carbon signals at δ_C 169.4, 168.8, 170.1, 170.4 and 169.1, respectively. These data indicated that the furanoyl group was assigned to position C-11 and the five acetyl groups were assigned to the positions C-1, C-2, C-5, C-7 and C-8, respectively. On the other hand, the proton signal at δ_H 2.47 (8′-H) was correlated with the carbon signals at δ_C 173.9 (C-11′), 10.0 (C-10′), 33.4 (C-7′) and 156.6 (C-4′), the proton signals at δ_H 7.37 (5′-H) with the carbon signals at δ_C 153.0 (C-6′), 125.4 C-3′) and 33.4 (C-7′), these facts indicated that the pyridyl unit was 2,3-dimethyl-3-(3′-carboxy-4′-pyridyl)-propanoic acid. The dihydroagrafuran core linked with this pyridyl unit by ester linkage at position C-3 and C-15 from HMBC spectrum of **4**. The remaining proton and carbon signals were assigned as shown in Tables 1 and 2 by using 2D NMR and NOESY. Therefore, the structure of hypoglaunine D (**4**) was formulated as shown.

Compounds **5**, **6**, **7**, **8** and **9** were identified from spectral data comparison to be wilforine [11], wilforgine [11], wilfordine [15], wilfortrine [13] and euonymine [12], respectively.

EXPERIMENTAL

NMR experiments were run on a ARX-400 instrument, ^1H-NMR: 400 MHz with TMS as int. standard; ^{13}C NMR: 100 MHz. MS were obtained on a JEOL JMSD-300 instrument, chromatography column: silica gel and Sephadex LH-20, Toyopearl HW-40 (TOSOH), HPLC: GPC (Asahipak, GS-310 2G, MeOH), silica gel HPLC (Si6O, Hibar RT 250-25), ODS_1 (YMC packed column SH-345-5, S-5, Yamamura, Japan), ODS_2 [Hibar RT 250-25 LiChrosorb RP-18 (7 μm)], ODS_3 (INERTSIL PREP ODS, 20.0 × 250 mm, GL Sciences).

Plant material

The root outer barks of *Tripterygium hypoglaucum* (Levl.) Hutch were purchased in 1995 from Kunming of Yunnan province in China.

Extraction and isolation

The root outer barks (15.3 kg) of *T. hypoglaucum* were crushed and extracted 3× with MeOH (50 l each) at 60°C for 6 h. 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 a solvent of increasing polarity [hexane–EtOAc (3:1, 3:2, 1:1, 1:2, 1:4), EtOAc, EtOAc–MeOH (19:1, 9:1, 4:1) and MeOH] to give 22 frs (fr. 1–22). Fr. 14 + 15 (60 g) was chromatographed on silica gel with $CHCl_3$–MeOH (19:1, 9:1, 8:2) and MeOH to give 10 frs (fr. 14.1–14.10). Fr. 14.2 (18 g) was chromatographed on middle pressure silica gel column with $CHCl_3$–MeOH system to give 9 frs (fr. 14.2.1–14.2.9). Fr. 14.2.7 (5.8 g) was dissolved in MeOH–H_2O (8:2) and the dissolved portion was chromatographed by using HPLC (ODS_1, MeOH–H_2O, 8:2) to give 7 frs (fr. 14.2.7.1–14.2.7.7). Fr. 14.2.7.3 (1.5 g) was separated on CC using HPLC (ODS_1, MeOH–H_2O, 7:3) to give 5 frs (fr. 14.2.7.3.1–14.2.7.3.5). Fr. 14.2.7.3.4 was separated on CC using HPLC (GPC, recycle) to give **1** (95 mg) and fr. 14.2.7.3.4.2. 30 mg of this fr. was subjected to recycle GPC to afford **1** (10 mg) and **2** (14 mg). Fr. 14.2.7.5 was separated on CC using HPLC (ODS_3, MeOH:H_2O, 8:2) to give **3** (37 mg), **7** (28 mg) and another six frs (fr. 14.2.7.1–14.2.7.6). Fr. 14.2.7.4 and 14.2.7.6 were separated on CC using Si60 ($CHCl_3$–MeOH, 99:1) to give **6** (36 mg) and **5** (19 mg), respectively.

Fr. 14.2.8 (570 mg) was separated on CC using GPC (MeOH) and ODS_2 (MeOH:H_2O, 8:2) to give **8** (165 mg). Fr. 14.2.4 (2 g) was separated on CC using ODS_3 (MeOH:H_2O, 8:2) to give **9** (490 mg) and fr. 14.2.4.1–14.2.4.10. Fr. 14.2.4.7 was separated on CC using ODS_3 (MeOH:H_2O, 7:3) to give **6** (310 mg) and 4 frs (fr. 14.2.4.7.1–14.2.4.7.4), further more, fr. 14.2.4.7.3 were separated by Si60 ($CHCl_3$:MeOH, 99:1) to give **4** (35 mg).

*Hypoglaunine A (**1**)*

Amorphous powder, $[\alpha]_D^{25}$ +42.8° (MeOH *c* 1.0). IR ν_{max}^{KBr} cm^{-1}: 3631, 3449, 1747, 1594, 1510, 1373, 1309, 1231, 1162, 1122, 1045, 875, 762, 605. UV λ_{max}^{MeOH} nm (log ε): 256 (3.86). ^1H NMR: δ ($CDCl_3$): see Table 1. ^{13}C NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 873 $[M]^+$ (100), 858 $[M–CH_3]^+$ (4), 814 $[M–OCOCH_3]^+$ (11), 748 (7), 710 (3), 194 (3), 176 (7), 150 (7), 134 (7), 107 (4), 95 (14), 44 (63). HR EI-MS *m/z* 873.2703 $[M]^+$, $C_{41}H_{47}O_{20}N$ required 873.2691.

*Hypoglaunine B (**2**)*

Amorphous powder, $[\alpha]_D^{25}$ +46.2° (MeOH *c* 0.8). IR ν_{max}^{KBr} cm^{-1}: 3631, 3622, 3569, 3449, 2371, 2346, 1752, 1687, 1656, 1639, 1459, 1376, 1236, 1157, 1122, 1047, 707. UV λ_{max}^{MeOH} nm (log ε): 262 (3.82). ^1H NMR: δ ($CDCl_3$): see Table 1. ^{13}C NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 873 $[M]^+$ (95), 814 $[M–OCOCH_3]^+$ (17), 779 (85), 748 (11), 720 (17), 246 (11), 222 (25), 206 (27), 194 (27), 176 (60), 161 (18), 150 (65), 134 (60), 107 (52), 95 (65), 83 (12), 69 (18), 55 (23), 43 (100). HR-EIMS *m/z* 873.2692 $[M]^+$ $C_{41}H_{47}O_{20}N$ required 873.2691.

*Hypoglaunine C (**3**)*

Amorphous powder, $[\alpha]_D^{25}$ +56.7° (MeOH *c* 1.0). IR ν_{max}^{KBr} cm^{-1}: 3652, 3432, 1746, 1638, 1459, 1372, 1234, 1156, 1096, 1051, 715, 603. UV λ_{max}^{MeOH} nm (log ε): 230 (4.26), 265(3.65). ^1H NMR: δ ($CDCl_3$): see Table 1. ^{13}C NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 883 $[M]^+$ (100), 824 $[M–OCOCH_3]^+$ (13), 810 (7), 208 (5), 194 (8), 176 (18), 150 (16), 134 (14), 105 (67), 77 (8), 43 (32), 28 (45), 18 (38). HR EI-MS *m/z* 883.2913 $[M]^+$ $C_{43}H_{49}O_{19}N$ required 883.2899.

*Hypoglaunine D (**4**)*

Amorphous powder, $[\alpha]_D^{25}$ −15.3° (MeOH *c* 0.9). IR ν_{max}^{KBr} cm^{-1}: 3652, 3631, 3449, 2366, 1752, 1639, 1372, 1234, 1121, 1058, 899, 601. UV λ_{max}^{MeOH} nm (log ε): 226 (3.82), 264 (3.42). ^1H NMR: δ ($CDCl_3$): see Table 1. ^{13}C NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 857 $[M]^+$ (47), 842 $[M–CH_3]^+$ (30), 798 $[M–OCOCH_3]^+$ (32), 745 (10), 732 (34), 686 (28), 258 (20), 220 (33), 178 (99), 79 (100), 28 (66). HR EI-MS *m/z* 857.2739 $[M]^+$ $C_{41}H_{47}O_{19}N$ required 857.2742.

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