Sesquiterpene Alkaloids from Extracts of *Tripterygium wilfordii*

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Received July 5, 1999; accepted August 12, 1999

Five new sesquiterpene pyridine alkaloids, named wilfordinines D (1), E (2), F (3), G (4) and H (5), along with six known compounds have been isolated from the extracts (T_{II}) of *Tripterygium wilfordii* HOOK F. Their structures were elucidated by spectroscopy.

Key words *Tripterygium wilfordii*; Celastraceae; sesquiterpene; wilfordinine

The genus of *Tripterygium* (*T.*) has been used in traditional Chinese drugs for the treatment of cancer and as an insecticide for hundreds of years. In the course of our studies on the bioactive metabolites of this genus, we have isolated and determined the structures of triptonine A and hypoglaunine B from *T. hypoglaucum*, as well as investigating their anti-human immunodeficiency virus (HIV) activity,[1] and have also reported the isolation and structure determination of wilforic acid A, B and C from *T. wilfordii* HOOK F.[2] Recently, an extract of the roots of *T. wilfordii* HOOK F. (the so-called total multi-glycoside or T_{II}) has been used in the clinical treatment of rheumatoid arthritis, skin disorders, in male-fertility control and other inflammatory and autoimmune diseases.[3—5] The precise mechanism of the therapeutic effect of T_{II}, however, is not completely understood. In order to determine which of the components present in the extracts (T_{II}) are responsible for such diverse activities, we started work on the isolation of the active principles of the extract (T_{II}) of *T. wilfordii*. In this paper, we report the isolation and structure elucidation of five new sesquiterpene alkaloids, named wilfordinines D (**1**), E (**2**), F (**3**), G (**4**), H (**5**) and six known compounds (**6**—**11**) from T_{II}.

Powdered extracts (T_{II}) of *T. wilfordii* HOOK F. were separated by repeated silica gel column chromatography, HPLC and gel permeation chromatography (GPC), to give compounds **1**—**11**.

Wilfordinine D (**1**) was obtained as an amorphous solid and its mass spectrum showed the molecular ion peak at *m/z* 857. The IR spectrum showed hydroxyl and ester carbonyl bands (3436 and 1742 cm^{-1}), and its UV absorption spectrum indicated the presence of an aromatic ring (227 and 261 nm). Compound **1** contained five acetyl groups [δ_H 1.84, 1.98, 2.30 (each 3H, s) and 2.18 (6H, s)], one furanoyl group (Fu) [δ_H 6.85 (d, 1.4), 7.49 (br s) and 8.27 (s)], four sets of methylene groups [δ_H 1.65, 2.35 (each 1H, m), 2.69, 3.89 (each 1H, m), 3.78, 5.82 (each 1H, d, 11.9); 4.29, 5.51 (each 1H, d, 13.5)] and eight methine protons [δ_H 2.34, 2.37, 5.01, 5.36, 5.42, 5.55, 5.70, 6.97]. Compound **1** also contained one pyridine ring [δ_H 9.22 (s), 8.68 (d, 5.1) and 7.26 (d, 5.1)] from the ^{1}H-NMR spectral data. Due to the presence of six ester groups and a pyridine ring, **1** was assumed to be a sesquiterpene pyridine alkaloid derivative, one of the dihydroagarofuran polyol esters, similar to wilfordate type sesquiterpenes.[6] By comparing ^{13}C-NMR spectral data of **1** and isowilfordine (**6**),[7] compound **1** was found to be similar to **6**, except for the ester group and the C-9′ hydroxyl group in **6** (Table 2).

From the ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY spectrum of **1**, a partial structure [–$CH_2CH_2CH(CH_3)$–] was determined. Further more, the proton signal at δ_H 3.89 (7a′-H) correlated with the carbon signal at δ_C 124.5 (C-3′); the signal at δ_H 7.26 (5′-H) correlated with the signals at δ_C 153.4 (C-6′), 155.1 (C-4′), 124.5 (C-3′) and 29.7 (C-7′); the signal at δ_H 1.19 (10′-H_3) correlated with the signal at δ_C 174.6 (C-11′) in the HMBC spectrum. From these facts, an isowilfordic acid unit containing a 3, 4-substituted pyridine was deduced. In addition, the proton signals at δ_H 3.78 (15_b-H) and 9.22 (2′-H) correlated with the carbonyl carbon (δ_C 166.7), and the signal at δ_H 5.01 (3-H) with the carbonyl carbon (δ_C 174.6). Thus, the isowilfordic acid unit was linked by ester bonds to the dihydroagarofuran core at positions C-3 and 15.

From the HMBC spectrum of **1**, the locations of ester groups were determined as follows: the proton signals at δ_H 5.70 (1-H), 6.97 (5-H), 5.55 (7-H), 5.42 (8-H) and 5.51 (11_a-H) showed long-range correlation with the carbonyl carbon of the acetyl group at δ_C 169.3, 170.0, 170.1, 169.1 and 170.8, respectively. Also, the proton signal at δ_H 5.36 (2-H) correlated with the carbonyl carbon of the furanoyl group in the HMBC spectrum. Thus, the five acetyl groups were assigned at positions C-1, 5, 7, 8 and 11; and the furanoyl group was assigned at position C-2. In the nuclear Overhauser effect spectroscopy (NOESY) spectrum, the proton signal at δ_H 6.97 (5-H) correlated with the proton signals at δ_H 4.29 (11-H′) and 1.56 (12-H_3), the proton signal at δ_H 5.42 (8-H) with the δ_H 5.55 (7-H) and 5.70 (1-H), and the proton signal at δ_H 5.70 (1-H) with δ_H 5.42 (8-H) and 5.36 (2-H). This evidence indicated that the relative stereochemistry of the ester groups was 1β, 2β, 7β, 8β and 5α. Therefore, the structure of **1** was formulated as shown (Fig. 1).

Wilfordinine E (**2**), $C_{38}H_{47}O_{18}N$, contained six acetyl groups (δ_H 1.86, 2.00, 2.15, 2.17, 2.18 and 2.30), and a 3, 4-substituted pyridine ring [δ_H 9.21 (s); 7.25, 8.67 (each 1H, d, 5.1)]. It was also a macrocyclic sesquiterpene alkaloid and its ^{1}H-, ^{13}C-NMR spectral data were similar to those of **1**, except for the number of ester groups (**1**: Ac×5, Fu×1; **2**: Ac×6). In the HMBC spectrum, the proton signals at δ_H 5.61 (1-H), 5.15 (2-H), 6.94 (5-H), 5.53 (7-H), 5.37 (8-H) and 5.22 (11_a-H) correlated with the carbonyl carbon of the acetyl groups at δ_C 169.5, 169.0, 170.0, 170.2, 169.1 and 170.4, respectively. Therefore, the ester linking sites of the six acetyl groups were concluded to be C-1, 2, 5, 7, 8 and 11. The stereochemistry of the six acetyl groups of **2** was readily determined by the elucidation of the NOESY spectrum as described for **1**.

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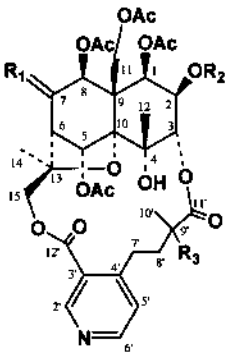
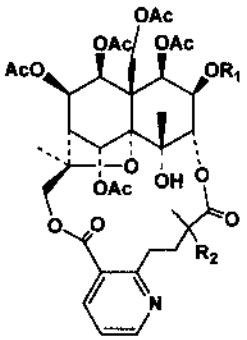
The ^{1}H-NMR spectrum of wilfordinine F (**3**), $C_{43}H_{49}O_{18}N$, revealed the presence of five acetyl groups (δ_H 1.85, 1.95, 2.18, 2.19, 2.20), and one benzoyl group [δ_H 8.09 (d, 7.3, *ortho*), 7.51 (br t, 7.5, *meta*), 7.63 (t, 7.5, *para*)]. The ^{13}C-NMR spectral data were similar to those of **1**, except for the ester groups (**1**: Ac×5, Fu×1; **3**: Ac×5, Bz×1). Compound **3** was also an isowilfordate type sesquiterpene alkaloid similar to **1**. According to the long-range correlation of the proton signal at δ_H 5.48 (2-H) with the carbonyl carbon of the benzonyl group (δ_C 165.1), the benzoyl group was located at C-2. The other acetyl groups were assigned as shown in the figure, in the same manner as described above.

Wilfordinine G (**4**) had a molecular formula $C_{36}H_{43}O_{18}N$, and its ^{1}H-NMR spectral data showed the presence of five acetyl groups (δ_H 1.93, 2.05, 2.12, 2.17, 2.22), and a 3, 4-substituted pyridyl unit [δ_H 9.01 (s), 8.64 and 7.25 (each 1H, d, 5.1)]. The ^{13}C-NMR spectral data showed eight methyl carbons, seven ester carbonyl carbons, five methine carbons attached to an oxygen function, two methylene carbons attached to an oxygen function, one carbonyl carbon (δ_C 196.0), and a hydroxy isowilfordic acid moiety [δ_C 27.3 (q), 77.2 (s), 40.3 (t), 28.4 (t), 155.3 (s), 125.6 (s), 151.1 (d), 153.2 (d), 125.9 (d), 167.8 (COO–), 172.0 (COO–)]. By comparing ^{13}C-NMR spectral data, the isowilfordic acid moiety was the same as that of **6**, and the dihydroagarofuran core was similar to that of **2**, except for the carbonyl group. In the HMBC spectrum, the proton signal at δ_H 6.77 (5-H) correlated with the carbon signals at δ_C 52.6 (C-9), 95.7 (C-10), 86.8 (C-13), 196.0 (C-7); the proton signals at δ_H 5.56 (8-H) and 3.05 (6-H) correlated with the carbonyl group (δ_C 196.0). Thus, the carbonyl group was allocated at C-7.

In addition, the proton signal at 1.48 (10′-H_3) correlated with the carbon signals at δ_C 77.2 (C-9′), 172.0 (C-11′) and 40.3 (C-8′), the proton signal at δ_H 4.99 (3-H) with the carbon signal at δ_C 172.0 (C-11′), and the proton signal at δ_H 5.95 (15_a-H) with the carbon signal at δ_C 167.8 (C-12′). From these facts, the presence of a hydroxy isowilfordic acid moiety was confirmed, and was linked by ester bonds to the dihydroagarofuran core at positions C-3 and 15. The location





	R_1	R_2	R_3
1	β-OAc, α-H	Fu	H
2	β-OAc, α-H	Ac	H
3	β-OAc, α-H	Bz	H
4	O	Ac	OH
5	β-OAc, α-H	Fu	OH
6	β-OAc, α-H	Bz	OH

	R_1	R_2
7	Fu	OH
8	Bz	OH
9	Ac	H
10	Ac	OH
11	Bz	H

Fig. 1

Table 1. ^{1}H-NMR Chemical Shifts of Compounds **1**—**5**

Proton	**1**	**2**	**3**	**4**	**5**
1	5.70 (d, 3.8)	5.61 (d, 3.6)	5.75 (d, 3.8)	5.72 (d, 3.0)	5.69 (d, 3.6)
2	5.36 (dd, 2.5, 3.8)	5.15 (dd, 2.5, 3.6)	5.48 (br, 2.6, 3.8)	5.16 (dd, 3.0, 3.2)	5.35 (dd, 2.7, 3.6)
3	5.01 (d, 2.5)	4.92 (d, 2.5)	5.06 (d, 2.6)	4.99 (d, 3.2)	5.02 (d, 2.7)
5	6.97 (s)	6.94 (s)	6.94 (s)	6.77 (s)	6.94 (s)
6	2.34 (d, 4.1)	2.34 (d, 3.9)	2.37 (d, 4.1)	3.05 (s)	2.38 (d, 3.8)
7	5.55 (dd, 4.1, 6.0)	5.53 (dd, 3.9, 6.0)	5.56 (dd, 4.1, 6.0)	—	5.54 (dd, 3.8, 5.9)
8	5.42 (d, 6.0)	5.37 (d, 6.0)	5.42 (d, 6.0)	5.56 (s)	5.41 (d, 5.9)
11a	5.51 (d, 13.5)	5.22 (d, 13.4)	5.51 (d, 13.3)	4.85 (d, 13.1)	5.55 (d, 13.4)
11b	4.29 (d, 13.5)	4.46 (d, 13.4)	4.40 (d, 13.3)	4.54 (d, 13.1)	4.31 (d, 13.4)
12	1.56 (s)	1.54 (s)	1.68 (s)	1.64 (s)	1.62 (s)
14	1.70 (s)	1.68 (s)	1.71 (s)	1.55 (s)	1.66 (s)
15a	5.82 (d, 11.9)	5.80 (d, 12.0)	5.82 (d, 12.0)	5.95 (d, 12.0)	5.87 (d, 12.1)
15b	3.78 (d, 11.9)	3.77 (d, 12.0)	3.80 (d, 12.0)	3.76 (d, 12.0)	3.74 (d, 12.1)
2′	9.22 (s)	9.21 (s)	9.22 (s)	9.01 (s)	9.00 (s)
5′	7.26 (d, 5.1)	7.25 (d, 5.1)	7.27 (d, 5.1)	7.25 (d, 5.1)	7.24 (d, 5.1)
6′	8.68 (d, 5.1)	8.67 (d, 5.1)	8.68 (d, 5.1)	8.64 (d, 5.1)	8.63 (d, 5.1)
7a′	3.89 (m)	3.87 (m)	3.87 (m)	3.93 (m)	3.93 (m)
7b′	2.69 (m)	2.68 (m)	2.70 (m)	2.62 (m)	2.63 (m)
8a′	2.35 (m)	2.35 (m)	2.35 (m)	2.37 (m)	2.46 (m)
8b′	1.65 (m)	1.60 (s)	1.67 (m)	1.97 (m)	1.93 (m)
9′	2.37 (m)	2.34 (m)	2.42 (m)	—	—
10′	1.19 (d, 6.3)	1.17 (d, 6.4)	1.21 (d, 6.8)	1.48 (s)	1.47 (s)
1-OAc	1.84 (s)	1.86 (s)	1.85 (s)	1.93 (s)	1.87 (s)
2-OAc	—	2.15 (s)	—	2.17 (s)	—
5-OAc	2.18 (s)	2.17 (s)	2.18 (s)	2.22 (s)	2.19 (s)
7-OAc	2.30 (s)	2.30 (s)	2.19 (s)	—	2.26 (s)
8-OAc	1.98 (s)	2.00 (s)	1.95 (s)	2.12 (s)	1.98 (s)
11-OAc	2.18 (s)	2.18 (s)	2.20 (s)	2.05 (s)	2.20 (s)

1. 2-Fu: 8.27 (s), 6.85 (d, 1.4), 7.49 (br s); **3**. 2-Bz: 8.09 (d, 7.3, *ortho*), 7.51 (br t, 7.5, *meta*), 7.63 (t, 7.5, *para*); **5**. 2-Fu: 8.27 (s), 6.84 (d, 1.4), 7.50 (d, 1.4).

Table 2. ^{13}C-NMR Spectral Data of Compounds **1**—**5**

Carbon	**1**	**2**	**3**	**4**	**5**	**6**
1	73.5	73.8	73.6	72.6	73.1	73.3
2	69.2	69.4	69.8	68.8	68.7	69.2
3	76.1	76.3	76.2	76.6	76.8	77.0
4	69.9	70.1	69.9	70.3	69.9	69.8
5	73.7	73.9	73.7	73.6	73.6	73.6
6	51.4	51.4	51.3	62.5	51.3	51.1
7	69.0	69.2	69.1	196.0	68.9	68.9
8	70.8	71.0	70.9	78.3	70.7	70.7
9	52.2	52.3	52.2	52.6	52.4	51.9
10	94.0	94.0	93.9	95.7	94.3	94.1
11	60.5	60.3	60.6	60.4	60.5	60.5
12	22.9	22.8	23.1	23.5	22.8	23.0
13	84.7	84.8	84.7	86.8	85.0	84.9
14	18.0	18.1	18.0	18.8	17.9	17.8
15	70.5	70.6	70.5	70.2	70.0	69.9
2′	152.0	152.1	152.0	151.1	150.9	150.8
3′	124.5	124.6	124.6	125.6	126.0	125.9
4′	155.1	155.1	155.0	155.3	155.4	155.2
5′	126.4	126.5	126.4	125.9	125.7	125.6
6′	153.4	153.5	153.4	153.2	152.9	152.7
7′	29.7	29.8	29.8	28.4	28.1	28.0
8′	34.8	34.9	34.8	40.3	39.4	39.8
9′	38.0	38.1	38.0	77.2	77.6	77.6
10′	18.9	19.0	18.9	27.3	28.0	27.7
11′	174.6	174.8	174.7	172.0	172.1	172.1
12′	166.7	166.8	166.8	167.8	167.9	167.7
1-OAc	20.6	20.7	20.5	20.6	20.5	20.5
	169.3	169.5	169.5	169.8	169.8	170.0
2-OAc	—	21.2	—	21.1	—	—
	—	169.0	—	168.6	—	—
5-OAc	21.1	21.2	21.2	21.5	21.1	21.6
	170.0	170.0	170.0	169.4	169.9	169.8
7-OAc	21.3	21.5	21.1	—	21.2	21.0
	170.1	170.2	170.1	—	170.7	170.2
8-OAc	20.6	20.7	20.6	20.3	20.6	20.5
	169.1	169.1	169.1	169.5	169.1	169.0
11-OAc	21.7	21.8	21.7	20.7	21.6	21.1
	170.8	170.4	170.4	169.9	170.1	170.0

1. 2-Fu: 161.1, 148.8, 118.4, 109.8, 144.3; **3**. 2-Bz: 165.1, 128.8 (*ipso*), 130.2 (*ortho*), 128.8 (*metha*), 133.8 (*para*); **5**. 2-Fu: 161.0, 148.8, 118.2, 109.8, 144.4.

and relative configuration of the five acetyl groups were assigned as C-1β, 2β, 8β, 5α and 11 by studying the HMBC and NOESY spectra of **4**. Therefore, **4** was determined as shown (Fig. 1).

Wilfordinine H (**5**), $C_{41}H_{47}O_{20}N$, had similar ^{1}H-, ^{13}C-NMR spectral data to that of **1** (Tables 1 and 2). Compound **5** was also a hydroxy isowilfordic acid type sesquiterpene alkaloid similar to **6** and had the same ester groups as **1**. The HMBC correlation showed the assignments of the five acetyl groups were at C-1, 5, 7, 8 and 11. In addition, the proton signal at δ_H 5.35 (2-H) correlated with the carbonyl carbon of the furanoyl group (δ_C 161.0). Thus, the furanoyloxy group was at C-2.

By comparing spectral data, the known compounds **6**—**11** were identified as follows: isowilfordine (**6**),[7] wilfortrine (**7**),[6] wilfordine (**8**),[6] euonine (**9**),[8] alatusinine (**10**),[9] wilforine (**11**).[6]

Experimental

General Experimental Procedures NMR experiments were run on a Bruker ARX-400 instrument. ^{1}H-NMR, 400 MHz; ^{13}C-NMR, 100 MHz, both use tetramethylsilane as internal standard. MS were obtained on a JEOL JMSD-300 instrument. Chromatography column, Silica gel 60 (Merck) and Sephadex LH-20 (Pharmacia); HPLC, JASCO Gulliver Series, PU-986/987 (pump), RI930 and UV970 (detector). Column type, LiChrosorb Si 60 HPLC (Hibar RT 250-25, 20.0×250 mm, Kanto Chemical Co., Inc.), ODS (INERTSIL PREP ODS, 20.0×250 mm, GL Sciences Inc.). IR spectra were recorded on a 1720 Infrared Fourier Transform spectrometer (Perkin-Elmer), UV spectra on a UV 2100 UV-VIS recording spectrometer (Shimadzu). Optical rotation were measured with a JASCO DIP-370 digital polarimeter.

Plant Material The powdered extracts of *Tripterygium wilfordii* (T_{II}) were purchased in 1997 from the School of Pharmacy, Shanghai Medical University, China. By extraction of the root xylem with water, then chloroform, was followed by column chromatography.

Extraction and Isolation The extracts (T_{II}, 54 g) of *T. wilfordii* were chromatographed on a silica gel column (1.0 kg, 11×90 cm) and eluted with a solvent of increasing polarity [$CHCl_3$–MeOH (99 : 1, 95 : 5, 9 : 1, MeOH)] to give ten fractions (fr. 1—10). Fraction 5 (16.5 g) was chromatographed on a silica gel column (6×80 cm) and eluted with hexane–EtOAc (1 : 1, 1 : 2, 1 : 4) to give twelve fractions (frs. 5.1—5.12). Fraction 5.9 (3 g) was chromatographed on LH-20 (MeOH) to afford five fractions (frs. 5.9.1—5.9.5). Fraction 5.9.1 (2 g) was chromatographed on an ODS column (MeOH : H_2O, 8 : 2) to give 8 fractions (frs. 5.9.1.1—5.9.1.8). Fraction 5.9.1.1 was separated by HPLC (ODS, MeOH : H_2O, 7 : 3) and then Si 60 chromatography to give **4** (13 mg) and **10** (134 mg). Fraction 5.9.1.2 was separated by Si 60 ($CHCl_3$: MeOH, 99 : 1) and ODS (MeOH : H_2O, 7 : 3) to give **2** (5.5 mg) and **9** (77 mg). Fraction 5.9.1.3 was separated by HPLC (Si 60, $CHCl_3$: MeOH, 99 : 1) to give **5** (8.5 mg) and **7** (13 mg). Fraction 5.9.1.5 was chromatographed on ODS (MeOH : H_2O, 7 : 3) to give **1** (4 mg), **8** (14 mg) and **11** (74 mg). Fraction 5.9.1.7 was chromatographed on HPLC (Si 60, $CHCl_3$: MeOH, 99 : 1) to give **3** (14 mg) and **6** (16 mg).

Wilfordinine D (1) Amorphous powder, $[\alpha]_D^{25}$ +14.6° (c=0.4, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3570, 3436, 2921, 2853, 1742, 1656, 1639, 1562, 1510, 1460, 1376, 1233, 1116, 600. UV λ_{max}^{MeOH} nm (log ε): 227 (4.06), 261 (3.57). ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 857 $[M]^+$ (24), 842 $[M-Me]^+$ (18), 798 $[M-OCOMe]^+$ (17), 784 (19), 206 (51), 178 (32), 164 (13), 160 (25), 150 (16), 132 (22), 119 (13), 105 (32), 93 (100), 43 (36). HR-EIMS *m/z*: 857.2712. $C_{41}H_{47}O_{19}N$ required 857.2742.

Wilfordinine E (2) Amorphous powder, $[\alpha]_D^{25}$ −0.6° (c=0.7, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3570, 3437, 1752, 1687, 1656, 1639, 1630, 1562, 1459, 1421, 1371, 1234, 1112, 1047, 761. UV λ_{max}^{MeOH} nm (log ε): 225 (3.98), 264 (3.50). ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 805 $[M]^+$ (29), 790 $[M-Me]^+$ (29), 746 $[M-OCOMe]^+$ (30), 732 (35), 206 (54), 178 (36), 164 (17), 160 (26), 150 (15), 132 (23), 124 (21), 105 (27), 93 (100), 43 (55). HR-EIMS *m/z*: 805.2816. $C_{38}H_{47}O_{18}N$ required 805.2793.

Wilfordinine F (3) Amorphous powder, $[\alpha]_D^{25}$ +16.2° (c=0.9, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3570, 3435, 1752, 1687, 1656, 1639, 1562, 1510, 1476, 1459, 1371, 1232, 1096, 1049, 714. UV λ_{max}^{MeOH} nm (log ε): 230 (4.32), 265 (3.55). ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 867 $[M]^+$ (100), 852 $[M-Me]^+$ (53), 808 $[M-OCOMe]^+$ (46), 794 (45), 750 (11), 206 (29), 178 (17), 160 (15), 132 (14), 105 (75), 93 (45), 43 (16). HR-EIMS *m/z*: 867.2949. $C_{43}H_{49}O_{18}N$ required 867.2950.

Wilfordinine G (4) Amorphous powder, $[\alpha]_D^{25}$ +4.3° (c=1.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3652, 3464, 2935, 1752, 1639, 1594, 1561, 1372, 1235, 1046, 1009, 760, 600. UV λ_{max}^{MeOH} nm (log ε): 221 (3.89), 263 (3.47). ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 777 $[M]^+$ (31), 762 $[M-Me]^+$ (11), 748 (14), 718 $[M-OCOMe]^+$ (39), 704 (31), 690 (10), 614 (17), 250 (28), 222 (18), 206 (28), 194 (57), 176 (100), 164 (16), 150 (45), 134 (26), 107 (33), 93 (19), 43 (69). HR-EIMS *m/z*: 777.2498. $C_{36}H_{43}O_{18}N$ required 777.2480.

Wilfordinine H (5) Amorphous powder, $[\alpha]_D^{25}$ +1.4° (c=0.7, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3570, 3431, 1752, 1656, 1639, 1562, 1510, 1460, 1371, 1234, 762. UV λ_{max}^{MeOH} nm (log ε): 227 (4.10), 262 (3.57). ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. EI-MS *m/z* (rel. int.): 873 $[M]^+$ (51), 858 $[M-Me]^+$ (16), 841 (13), 814 $[M-OCOMe]^+$ (24), 800 (27), 852 (25), 250 (20), 222 (11), 206 (13), 194 (63), 176 (94), 164 (17), 150 (45), 134 (29), 105 (58), 95 (100), 44 (85). HR-EIMS *m/z*: 873.2743. $C_{41}H_{47}O_{20}N$ required 873.2691

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