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NORDITERPENOID ALKALOIDS FROM *DELPHINIUM SIWANENSE* VAR. *LEPTOGEN*

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Key Word Index—*Delphinium siwanense* var. *leptogen*; Ranunculaceae; norditerpenoid alkaloids; siwanine A, B, C, D.

Abstract—Four norditerpenoid alkaloids, siwanine A–D, together with the known tatsiensine have been isolated from the aerial parts of *Delphinium siwanense* var. *leptogen* (H.-M.) W. T. Wang. Their structures were elucidated on the basis of NMR spectroscopy and X-ray experiments. © 1998 Elsevier Science Ltd. All rights reserved

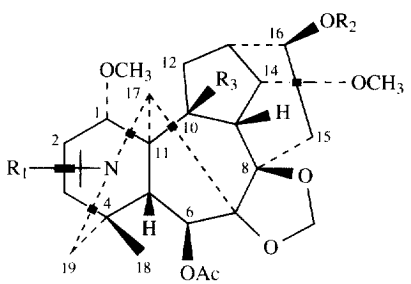
INTRODUCTION

The majority of phytochemical studies of *Aconitum*, *Delphinium* and *Consolida* genera (Ranunculaceae), the main sources of diterpenoid alkaloids, have been carried out with species from Asia, Europe and North America. *Delphinium siwanense* var. *leptogen* (H.-M.) W. T. Wang is widely distributed in the northwest part of China, and no phytochemical investigations of it have yet been reported. In this paper, we report the isolation and structure elucidation of four new norditerpenoid alkaloids, siwanine A (**1**), siwanine B (**2**), siwanine C (**3**) and siwanine D (**4**) from the aerial parts of this plant. The complete ^{1}H NMR chemical shifts of one known tatsiensine (**5**) are also assigned.

RESULTS AND DISCUSSION

The crude alkaloid mixture from air-dried and powdered aerial parts of *Delphinium siwanense* var. *leptogen* was subjected to chromatography on alumina to afford eight fractions I–VIII which were further purified to yield siwanine A (**1**), B (**2**), C (**3**), D (**4**) and the known tatsiensine (**5**) [1].

Siwanine A (**1**) was obtained as an amorphous powder and the molecular formula $C_{27}H_{39}NO_8$ was derived from its HREI and FAB mass spectra. The IR spectrum of **1** displayed the presence of ester carbonyl (1739 cm^{-1}) and hydroxyl (3529 cm^{-1}) groups. The ^{1}H NMR spectrum (Table 2) of **1** indicated the presence of three methoxyl groups (δ_H 3.33 *s*, 3.34 *s* and 3.44 *s*), a tertiary methyl group (δ_H 1.00 *s*), an *N*-ethyl group (δ_H 1.07, *t*, J = 7.2 Hz), an acetoxy group (δ_H 2.08 *s*), and a methylenedioxy group (δ_H 4.84 *s*, 4.98 *s*). The ^{13}C NMR and DEPT spectrum (see Table 1) of **1** revealed the presence of six quaternary, six methyl, five methylene, and 10 methine carbons, representing the 27 carbon atoms of the molecule. These spectral data suggested that **1** was a norditerpenoid alkaloid, $C_{19}H_{19}(OCH_3)_3(OH)(OCOCH_3)(OCH_2O)(N\text{-}CH_2CH_3)$. The NMR spectrum of **1** was similar to those of **5** [1] and deltaline [2]. Two olefin proton doublets at δ_H 5.68 ppm (*d*, $J_{2,3}$ = 10.0 Hz) and δ_H 5.99 ppm (*dd*, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 4.0 Hz) in the ^{1}H NMR spectrum, combined with two olefinic carbon



1 R_1 = Et, R_2 = CH_3, R_3 = OH

2 R_1 = Et, R_2 = H, R_3 = OH

3 R_1 = CH_3, R_2 = CH_3, R_3 = H

4 R_1 = CH_3, R_2 = H, R_3 = OH

5 R_1 = Et, R_2 = CH_3, R_3 = H

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Table 1. ^{13}C NMR chemical shift assignments (ppm) of Siwanine A (**1**)–D (**4**) and tatsiensine (**5**)

C	1	2	3	4	5	5*
1	75.9	75.7	80.0	75.9	79.9	83.6
2	125.2	124.8	124.4	124.5	124.4	124.6
3	137.9	137.0	137.2	137.6	137.2	137.4
4	34.7	34.5	34.5	34.6	34.6	34.8
5	50.0	49.7	54.1	49.0	54.2	54.8
6	78.9	79.0	78.2	78.7	78.3	78.5
7	90.9	91.2	91.5	91.5	91.1	91.3
8	82.2	81.7	84.4	81.4	84.1	84.3
9	50.4	48.5	47.4	48.5	47.2	47.4
10	84.0	83.6	39.0	83.6	39.7	40.0
11	56.4	55.9	50.8	55.9	50.1	50.8
12	36.6	38.9	27.8	38.8	27.8	28.3
13	38.8	42.3	38.7	42.0	38.4	38.7
14	81.4	82.4	83.5	82.3	83.4	80.2
15	35.6	36.5	34.2	36.5	33.9	34.2
16	81.7	71.7	81.9	71.6	81.1	81.9
17	60.6	61.0	65.9	65.4	61.2	61.5
18	23.3	23.2	23.1	23.1	23.0	23.2
19	57.6	57.6	57.6	58.6	57.6	57.6
N-CH_2	48.5	48.5	43.6	43.4	48.5	48.7
CH_3	12.9	12.9	—	—	12.9	13.0
6-CO	169.6	169.6	168.6	169.5	169.7	169.9
CH_3	21.6	21.5	21.7	21.5	21.6	21.7
OCH_2O	94.1	93.9	93.7	93.9	93.4	93.4
1-OCH_3	55.8	56.0	56.2	56.6	55.7	55.9
14-OCH_3	57.6	57.8	58.7	57.6	57.4	57.6
16-OCH_3	56.1	—	56.4	—	56.0	56.2

* Previous shifts are from Pelletier [1].

Table 2. ^{1}H NMR chemical shift assignments (ppm) of siwanine A (**1**)–D (**4**) and tatsiensine (**2**)

Proton	1	2	3	4	5	Mult. *J*(Hz)
H-1	3.80	3.84	3.86	3.84	3.45	*d*, 4.0
H-2	5.99	5.99	6.01	5.98	5.97	*dd*, 4.0, 10.0
H-3	5.47	5.68	5.69	5.65	5.68	*d*, 10.0
H-5	1.73	1.86	1.58	1.62	1.54	*s*
H-6	5.47	5.47	5.50	5.47	5.42	*br s*
H-9	3.20	3.49	3.50	3.46	3.56	*m*
H-10	—	—	2.10	—	2.06	*m*
H-12	2.60, 1.80	2.70, 1.73	1.86, 2.52	1.73, 2.59	1.93, 2.25	*m*, *m*
H-13	2.50	2.49	2.60	2.49	2.40	*m*
H-14	4.13	4.24	4.26	4.25	3.71	*t*, 4.8
H-15	1.90, 2.53	2.66, 1.81	1.76, 2.62	1.82, 2.70	1.87, 2.47	*m*, *m*
H-16	2.97	3.65	3.64	3.64	3.26	*m*
H-17	3.19	3.15	2.99	3.15	3.10	*s*
H-18	1.00	0.99	1.00	0.99	1.00	*s*
H-19	2.47, 2.85	2.47, 2.65	2.50, 2.66	2.48, 2.67	2.52, 2.75	*m*, *m*
N-CH_2	2.55	2.56	2.53*s*	2.55*s*	2.55	*s*
CH_3	1.07	1.07	—	—	1.07	*t*, 7.2
$COCH_3$	2.08	2.07	2.10	2.05	2.05	*s*
OCH_2O	4.94, 4.98	4.91, 4.97	4.91, 4.99	4.93, 4.98	4.91, 4.98	*d*
1-OCH_3	3.33	3.32	3.35	3.31	3.31	*s*
14-OCH_3	3.44	3.47	3.48	3.45	3.41	*s*
16-OCH_3	3.34	—	3.36	—	3.34	*s*

signals at δ_C 125.2 (*d*, C-2) and δ_C 137.9 (*d*, C-3) in the ^{13}C NMR spectrum, suggested that the double-bond was located between the C-2 and C-3 positions [1, 3]. Long range correlations between C-1 and H-3, and C-3 and H-18 confirmed the presence of an olefin at C-2 and C-3. Three-bond couplings of H-6α with C-11,

Table 3. ^{1}H-^{1}H COSY, HMQC and HMBC correlations of siwanine A (**1**)–D (**4**)

Carbon	(HMQC)	^{1}H-^{1}H COSY	^{1}H-^{13}C Long-range correlation*
1	H-1	H-2	H-3, 1-OC<u>H</u>$_3$
2	H-2	H-1, H-3	H-1
3	H-3	H-2	H-1, H-18
4	—		H-2, H-3, H-6α
5	H-5		H-6, H-18, H-19
6	H-6		6-C<u>O</u>CH$_3$
7	—		H-6, OCH$_2$O
8	—		H-6, OCH$_2$O
9	H-9	H-14	H-12, H-13, H-15
10	—		H-1, H-12, H-13
11	—		H-1, H-2, H-6α, H-17
12	H-12	H-13	
13	H-13	H-12, 14	H-10, H-12, H-15
14	H-14	H-13, 9	14-OC<u>H</u>$_3$, H-12, H-16
15	H-15	H-16	
16	H-16	H-15, 13	H-12, H-14, H-15, 16-OCH$_3$
17	H-17		H-1
18	H-18		H-3
19	H-19		H-18
6-C<u>O</u>	C<u>H</u>$_3$		H-6α, COCH$_3$

* No HMBC correlation of C-16 and 16-OCH$_3$ protons in **2** and **4**.

C-4 and the ester carbonyl carbon were observed in the HMBC experiment (Table 3), and the broad singlet at δ_H 5.50 ppm attributable to H-6α, which was explained by a C-6/H-6 bond perpendicular to C-5/H-5 bond, revealed the presence of a β-acetoxyl group at C-6 [1, 4]. The IR spectrum of **1** exhibited a stronger absorption band for the hydroxyl group (3529 cm^{-1}). The main difference between **1** and **5** in their DEPT spectrum was that the methine carbon (δ_C 39.3 *d*) in **5** was replaced by a quaternary carbon (δ_C 84.0 *s*) bearing oxygen in **1**. This indicated that either the C-9 or C-10 position of **1** was substituted. The signal at δ_H 4.13 (*t*, J = 7.2 Hz) attributable to H-14 indicated that the C-9 site was not oxygenated [5]. Also, by comparison with the ^{13}C NMR spectral data of **1** and **5**, the assignments of the signals at C-10, C-9, C-11, and C-12 in **1** were found to have downfield shifts of *ca* 44.3, 3.2, 6.3 and 9.6 ppm, respectively. All of the aforementioned evidence supported structure **1** having a hydroxyl group at the C-10 position. Three methoxy groups were placed at C-1, C-14 and C-16 positions, based on the long-range connectivities of C-1 with 1-OCH$_3$, C-14 with 14-OCH$_3$ and C-16 with 16-OCH$_3$, respectively, in HMBC experiments. In the ^{1}H NMR spectrum of **1**, two oxygenated quaternary carbon signals at δ_C 90.0 *s* and 82.2 *s*, attributable to C-7 and C-8, respectively, indicated that the methylenedioxy group was located at C-7 and C-8, as usually found in norditerpenoid alkaloids [2]. Thus, the structure of **1** was assigned as 2,3-dehydrodeltaline.

Siwanine B (**2**) was obtained as an amorphous solid. The FAB mass spectrum of **2** showed the strong ion peak of $[M+1]^+$ at *m/z* 492 (50). The IR spectrum displayed the absorption bands for hydroxyl (3559 and 3443 cm^{-1}) and ester (1739 cm^{-1}) groups. The DEPT spectrum of **2** revealed the presence of six quaternary, five methyl, five methylene, and 10 methine carbon atoms. The ^{13}C and ^{1}H NMR spectra (Table 1 and 2) of **2** exhibited the characteristic signals of a tertiary methyl group at δ_H 0.99 *s*, (δ_C 23.2 *q*), an *N*-ethyl group at δ_H 1.07 (*t*, J = 7.1 Hz) (δ_C 12.9 *q*), a methylenedioxy group at δ_H 4.91 *s*, δ_H 4.97 *s* (δ_C 93.9 *t*), two methoxyl groups (δ_H 3.32 *s* and 3.47 *s*, δ_C 56.0 *q* and 57.8 *q*), an acetoxyl group at δ_H 2.07 *s* (δ_C 21.5 *q* and 169.6 *s*), and an unsubstituted olefin at δ_H 5.68 (*d*, J = 10.0 Hz) (δ_C 137.0 *d*) and δ_H 5.99 (*dd*, J = 4.0, 10.0 Hz) (δ_C 124.8 *d*). These spectral data indicated that **2** possessed the chemical formula $C_{19}H_{19}(OCH_3)_2(N\text{-}CH_2CH_3)(OCOCH_3)(OCH_2O)(OH)_x$ = 457 + 17x; thus x = 2 because the molecular weight of **2** is 491. Therefore the molecular formula $C_{26}H_{37}NO_8$ was deduced. The spectral data of **2** were very close to those of **1**, except that a 16-OCH$_3$ in **1** was replaced by a 16-OH in **2**. In the ^{1}H NMR spectrum of **2**, the chemical shift of the triplet at δ_H 4.24 ppm attached to H-14β indicated that C-9 and C-13 were not *O*-substituted, allowing us to place a tertiary hydroxyl group at C-10. The signals at δ_C 71.7 *d* and 42.3 *t* and δ_C 36.5 *t* were assigned to C-16, C-13 and C-15, respectively, based on the correlation of H-16 with H-15, H-13 in the ^{1}H-^{1}H COSY (Table 3), as well as the coupling of H-16 with C-16 in the HMQC experiment. Also the long-range couplings for C-14 (δ_C 82.4 *d*) and C-1 (δ_C 75.7 *d*) with the methoxyl protons in the HMBC spectrum (Table 3) supported that the two methoxyl groups were located at C-1 and C-14, respectively. Another OH group was located at C-16 (δ_C 71.7 *d*) on the basis of three-bond connectivities of C-

16 with H-12α and 12β in the HMBC experiment. Accordingly, the structure of **2** was assigned as 2,3-dehydroelasine (elasine reported in the literature [6]).

Siwanine C (**3**) was isolated as an amorphous glassy solid. The molecular formula $C_{26}H_{37}NO_7$ was derived from its FAB mass, ^1H and ^{13}C NMR and DEPT spectral data. The spectral data were very similar to those reported in the literature for tatsiensine (**5**) [1]. The IR spectrum of **3** showed the absorption band for an ester group (1740 cm^{-1}) and the absence of a hydroxyl band. The ^{13}C NMR spectra (Table 1) of **3** indicated the presence of five quaternary, six methyl, four methylene, and 11 methines, representing 26 carbon atoms of the molecule. The ^1H NMR spectrum (see Table 2) of **3** exhibited the presence of a tertiary methyl (δ_H 0.98 *s*), an *N*-methyl (δ_H 2.60 *s*), an acetoxyl (δ_H 2.06 *s*), a methylenedioxy (δ_H 4.92 *s* and 4.94 *s*), and three methoxyl (δ_H 3.35 *s*, 3.36 *s* and 3.42 *s*) groups. An unsubstituted olefin between C-2 (δ_C 124.4 *d*) (δ_H 6.01, *dd*, J = 10.0, 4.0 Hz) and C-3 (δ_C 137.2 *d*) (δ_H 5.69 *d*, J = 10.0 Hz) was deduced by taking into account the correlations from ^1H- COSY, HMQC and HMBC spectra. These spectral data suggested that **3** possessed the chemical formula $C_{19}H_{20}(OCH_3)_3$ (N-CH_3)(OCOCH_3)(OCH_2O). The long-range coupling between C-1 and 1-OCH_3 protons, C-14 and 14-OCH_3 protons, and C-16 and 16-OCH_3 protons were observed in its HMBC experiment, which supported that the three methoxyl groups were placed at C-1, C-14 and C-16, respectively. The coupling constant of H-6 with H-5 is very small (J < 1 Hz) and not resolved, indicating that the acetoxyl group at C-6 in **3** should have a β-orientation [1, 2]. Thus the structure of siwanine C (**3**) was easily determined as *N*-deethyl-*N*-methyltatsiensine [1].

Siwanine D (**4**) was found to have the molecular formula $C_{25}H_{35}NO_8$, by FAB mass, ^1H, ^{13}C and DEPT NMR spectroscopy. The ^{13}C and ^1H NMR spectra (Tables 1 and 2) of **4** indicated the presence of the following functional groups in the molecule: a tertiary methyl (δ_H 0.97 *s*, δ_C 23.1 *q*) an *N*-methyl (δ_H 2.55 *s*, δ_C 43.3 *q*), a methylenedioxy (δ_H 4.84 *s* and 4.95 *s*; δ_C 93.9 *t*), an acetyl (δ_H 2.05 *s*; δ_C 21.5 *q* and 169.5 *s*), two methoxy groups (δ_H 3.31 *s* and 3.45 *s*; δ_C 56.6 *q* and 57.6 *q*), and a methine (δ_H 4.23, *t*), J = 4.8 Hz; δ_C 82.3) [7]. These data showed that **4** is a norditerpenoid alkaloid. The molecular formula $C_{25}H_{35}NO_8$ indicated nine degrees of unsaturation, two of which were for the presence of one carbonyl and the C-7-C-8 methylenedioxy ring [3]. The skeleton of the norditerpenoid alkaloid possesses six degrees of unsaturation, so the remaining one degree of unsaturation indicated the presence of one double bond in **4**. The presence of resonances for two olefinic protons (δ_H 5.65, *d*, J = 10.0 Hz; δ_H 5.98, *dd* J = 10.0, 4.0 Hz) in the ^1H NMR of **4**, combined with the results of 2D shift-correlated HMQC, HMBC and ^1H-^1H COSY experiments (Table 3), indicated that the double bond is between C-2 and C-3. The ^1H NMR spectrum of **4** showed that it possessed a β-oriented acetoxyl group at C-6 (δ_H 5.46 *br s*) [1]. Its IR spectrum displayed absorption bands characteristic of hydroxy (3559 and 3543 cm^{-1}) and ester carbonyl group (1740 cm^{-1}), combined with the presence of seven oxygened carbon atoms (three quaternary and four methine carbons) in the ^{13}C NMR spectra, indicated the presence of two hydroxyl groups. The C-10 signal at δ 83.6 *s* (based on DEPT and 2D-NMR spectrum), and the shift upfield of the C-1 signal (*ca* 9 ppm) and downfield of C-11, C-12 (*ca* 6 ppm, 10 ppm, respectively) showed that there was a β-OH group at C-10 [2]. The signals at δ 71.6 *d*, 42.0 *d* and 36.5 *t* were assigned to C-16, C-13 and C-15, respectively, based on the ^1H-^1H COSY and HMBC spectra, which revealed a correlation of H-16 (δ 3.64 *m*) with H-13 and H-15. The other hydroxyl group was located at C-16 [6]. Three-bond connectivities of the C-1 carbon with 1-OCH_3 protons and the C-14 carbon with 14-OCH_3 protons were observed in HMBC experiment, indicating that the two hydroxyl groups were located at C-1 and C-14, respectively.

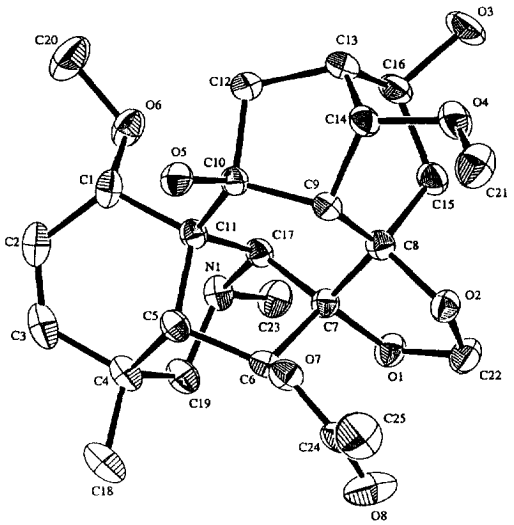

Fig. 1. The ORTEP drawing of Siwanine D (**4**) showing atomic labelling scheme.

An X-ray crystallographic analysis of **4** confirmed the structure and relative stereochemistry assigned from the foregoing evidence. The crystal structure was solved by direct methods [8]. The bond length between C-2 and C-3 was 1.312(5) Å and the hydroxyls at C-10 and C-16 were β-oriented. The ORTEP drawing is shown in Fig. 1.

The complete ^1H and ^{13}C NMR chemical shift assignments of tatsiensine **5** [1] were achieved by a study of its 2D ^1H-COSY, HMQC and HMBC spectra, resulting in revision of the assignments for C-1 and C-14 (see Table 1).

EXPERIMENTAL

General. Mp: uncorr. OR measured in $CHCl_3$. IR: KBr. FAB-MS was run on a VG ZAB-HS mass spectrometer. ^1H, ^{13}C and 2D-NMR in $CDCl_3$, with TMS

as int. standard. All solvents used were analytical grade. Al_2O_3 (neutral, 200–300 mesh) was used for CC.

Plant material. The aerial parts of *D. siwanense* var. *leptogen* were collected from Yu-zhong County, Gansu Province, People's Republic of China, in August 1992, and were identified by Dr Ji Ma, Department of Biology, Lanzhou University, People's Republic of China. A voucher specimen is deposited in the herbarium of the Department of Biology, Lanzhou University.

Extraction and isolation. The aerial parts of the plant (2 kg) were percolated with 95% EtOH (10 l) at room temp. The filtrates were combined and concd *in vacuo* to a dark green syrup, which was partitioned between $CHCl_3$ (500 ml) and aq. HCl (2%, 500 ml). The $CHCl_3$ phase was further extracted with aq. HCl (3 × 300 ml) until the last extracts showed only a very weak reaction when tested with Dragendorff's reagent. The acid soln was basified with NH_4OH to pH 11 and extracted repeatedly with $CHCl_3$ to give the crude alkaloid fr. This was chromatographed over Al_2O_3 (neutral) and eluted with petrol–Et_2O–EtOAc to afford eight frs I–VIII. Fr. I was further sepd by Al_2O_3 CC (petrol–Et_2O–Me_2CO 7:3:0.5) to yield **1** (40 mg) and **5** (18 mg). Further purification of fr. III on Al_2O_3 chromatography (Hexane–Et_2O–Me_2CO, 3:6:1) yielded **2** (180 mg) and **3** (20 mg). Fr. II was further purified on Al_2O_3 chromatography to yield **4** (50 mg).

Siwanine A (**1**). An amorphous powder, mp: 172–174° (EtOH); $[\alpha]_D$ +27.1° ($CHCl_3$, *c* 4.8). HREIMS (70 eV) *m/z*: 490.2458 $[M-CH_3]^-$, for $C_{26}H_{36}NO_8$ (calcd 490.2441), and 462.2505 $[M-CH_3CO]^+$, for $C_{25}H_{36}NO_7$ (calcd 462.2492). FABMS *m/z* (rel. int.): 506 $[M+1, 70]^+$ 504 (50), 490 (25), 474 (20), 462 (100), 446 (25) and 111 (90). IR ν_{max}^{KBr} cm^{-1}: 3529 (OH), 1739 ($OCOCH_3$), 1456, 1375, 1240, and 1086. For ^1H and ^{13}C NMR spectra see Tables 1 and 2.

Siwanine B (**2**). An amorphous solid, mp; 194–195° (EtOH); $[\alpha]_D$ −35.4° ($CHCl_3$; *c* 5.9). FAB-MS *m/z* (rel. int.): 492 $[M+1]^+$ (70), 490 (50), 474 (15), 461

Table 4. Atomic coordinates and B_{eq}

Atom	*x*	*y*	*z*	B_{eq}
O(1)	0.2045(1)	0.3151(1)	0.1076(2)	2.63(4)
O(2)	0.3409(1)	0.3365(1)	−0.0080(2)	2.56(4)
O(3)	0.3871(2)	0.6105(1)	0.1698(2)	3.98(6)
O(4)	0.5206(2)	0.4685(1)	0.0314(2)	3.36(5)
O(5)	0.5364(1)	0.2887(1)	0.3545(2)	2.75(5)
O(6)	0.3386(2)	0.3857(1)	0.5771(2)	3.26(5)
O(7)	0.3947(1)	0.1831(1)	0.1216(2)	2.63(4)
O(8)	0.2948(2)	0.1362(2)	−0.0307(3)	4.97(7)
N(1)	0.1890(2)	0.3062(2)	0.3987(2)	2.49(5)
C(1)	0.3766(2)	0.3040(2)	0.5312(3)	2.70(6)
C(2)	0.3345(3)	0.2319(2)	0.6076(3)	3.56(8)
C(3)	0.2850(3)	0.1684(2)	0.5580(3)	3.80(8)
C(4)	0.2646(2)	0.1615(2)	0.4173(3)	2.89(7)
C(5)	0.3474(2)	0.2021(2)	0.3414(3)	2.39(6)
C(6)	0.3175(2)	0.2115(2)	0.2022(3)	2.23(6)
C(7)	0.2852(2)	0.3084(2)	0.1889(3)	2.06(6)
C(8)	0.3560(2)	0.3671(2)	0.1222(3)	2.21(6)
C(9)	0.4559(2)	0.3509(2)	0.1700(3)	2.09(6)
C(10)	0.4545(2)	0.3383(2)	0.3197(3)	2.15(6)
C(11)	0.3641(2)	0.2973(2)	0.3841(3)	2.13(6)
C(12)	0.4755(2)	0.4320(2)	0.3696(3)	2.75(7)
C(13)	0.4785(2)	0.4919(2)	0.2533(3)	2.76(7)
C(14)	0.5198(2)	0.4312(2)	0.1543(3)	2.60(6)
C(15)	0.3294(2)	0.4647(2)	0.1223(3)	2.64(6)
C(16)	0.3792(2)	0.5233(2)	0.2186(3)	2.81(7)
C(17)	0.2722(2)	0.3366(2)	0.3295(3)	2.07(6)
C(18)	0.2504(3)	0.0666(2)	0.3800(4)	4.21(9)
C(19)	0.1737(2)	0.2125(2)	0.3888(3)	2.94(7)
C(20)	0.3885(3)	0.4154(3)	0.6856(3)	4.77(10)
C(21)	0.5671(3)	0.4162(3)	−0.0600(3)	4.25(9)
C(22)	0.2409(2)	0.3284(2)	−0.0183(3)	3.08(7)
C(23)	0.1024(2)	0.3531(2)	0.3662(4)	3.11(7)
C(24)	0.3739(3)	0.1490(2)	0.0071(3)	3.33(8)
C(25)	0.4603(3)	0.1306(3)	−0.0662(4)	5.00(1)

$B_{eq} = 8\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]/3$.

(10), 448 (100), 432 (20), 400 (15), 111 (60) and 77 (30). IR ν_{max}^{KBr} cm^{-1}: 3559, 3443 (OH), 1739 ($OCOCH_3$), 1452, 1336, 1247, 1080 and 1048. For ^1H and ^{13}C NMR spectra see Tables 1 and 2.

Siwanine C (**3**). An amorphous solid, $[\alpha]_D$ +9.6° ($CHCl_3$; FAB-MS *m/z* (rel. int.): 476 $[M+1]^+$ (40), 460 (4), 446 (5), 444 (4), 432 (15), 418 (2), 111 (40) and 77 (50). IR ν_{max}^{KBr} cm^{-1}: 1740 ($OCOCH_3$), 1452, 1364, 1246, 1081 and 1047. For ^1H and ^{13}C NMR spectra see Tables 1 and 2.

Siwanine D (**4**). Colourless crystals (EtOH), mp: 226–228°; $[\alpha]_D$ +30.2° ($CHCl_3$; *c* 0.1). FAB-MS *m/z* (rel. int.): 478 $[M+1]^+$ (70), 476 (50), 460 (15), 446 (8), 432 (15), 418 (10), 111 (55) and 77 (40). IR ν_{max}^{KBr} cm^{-1}: 3559, 3443 (OH), 1740 ($OCOCH_3$), 1450, 1365, 1247 and 1080. For ^1H and ^{13}C NMR spectra see Table 1.

Single Crystal X-ray Analysis of **4**. Diffraction data were collected with a Rigaku AFC 7 R diffractometer equipped with graphite monochromated *Mo-Kα* radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.56° < 2\theta < 21.35°$ corresponded to a primitive orthorhombic cell with dimensions. The data were collected at $20 \pm 1°$ using the ω-2θ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection had average width at half-height of 0.33° with a take-off angle of 6.0°. Scans of $(1.05 + 0.30 \tan\theta)°$ were made at a speed of 16.0° min^{-1} (in Omega). The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics.

The structure was solved by direct method (SPA 91) [8] and expanded using Fouler techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1884 observed reflections $[I < 3.00\sigma(I)]$ and 308 variable parameters and converged (largest parameter was 0.00 times its used) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.034$$

$$Rw = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2} = 0.038$$

All calculations were performed using the TeXsan crystallographic software package of Molecular Structure Corporation [9].

Crystal Data. $C_{25}H_{35}NO_8$, $FW = 477.55$, orthorhombic, space group $P\ 2_12_12_1$, $a = 14.144(1)$ Å, $b = 15.432(2)$ Å, $c = 10.500(2)$ Å, $V = 2290.5(5)$ Å^3, $Z = 4$, $Dc = 1.385$ g cm^{-1}, crystal size $0.20 \times 0.20 \times 0.40$ mm. For atomic coordinates see Table 4.

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