Sesterterpenoids, Terretonins A−D, and an Alkaloid, Asterrelenin, from *Aspergillus terreus*

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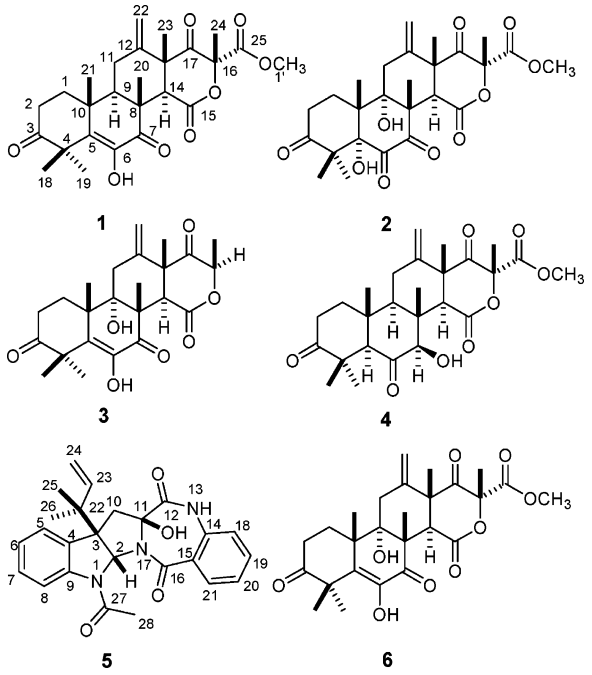
Four new sesterterpenoids, terretonins A−D (**1**−**4**), and a new alkaloid, asterrelenin (**5**), together with five known compounds, were isolated from the ethyl acetate extract of a solid-state fermented culture of *Aspergillus terreus*. Their structures were elucidated on the basis of spectroscopic analysis. The structures of **1**, **2**, and **5** were confirmed by X-ray crystallographic analysis.

Sesterterpenoids are a relatively small group of terpenoids found in terrestrial plants, insects, fungi, lichens, and marine organisms. Some sesterterpenes exhibit biological properties such as antiinflammatory,[1] cytotoxic,[2] antifeedant,[3] platelet aggregation,[4] and antimicrobial effects.[5] A few sesterterpenoids from the genus *Aspergillus* have been reported previously. Only one sesterterpene, terretonin (**6**), has been isolated from *A. terreus*.[6] In this study on *A. terreus*, four new terretonin derivatives, terretonins A (**1**), B (**2**), C (**3**), and D (**4**), and a new alkaloid, asterrelenin (**5**), were isolated, along with five known compounds, terretonin (**6**), butyrolactone A, butyrolactone B,[7] territrem A, and territrem B.[8] We herein report the isolation and structure determination of these compounds.



Results and Discussion

Compound **1** was isolated as colorless cubic crystals. Its molecular formula was determined to be $C_{26}H_{32}O_8$ from the HRESIMS quasi-molecular ion peak at *m/z* 471.2025 [M − H]$^-$. The IR spectrum suggested the presence of an OH group (3386 cm^{-1}). ^{13}C NMR signals (Table 1) at δ 213.8 (C-3), 201.3 (C-17), 166.9 (C-15), and 168.4 (C-25) indicated the presence of two ketone carbonyls and two ester carbonyls. An α,β-unsaturated ketone was suggested by the IR peaks at ν_{max} 1681 cm^{-1} and the ^{13}C NMR signal at δ 197.9. The ^{1}H NMR spectrum (Table 2) of **1** revealed a vinylidine moiety [δ 5.17 and 5.00 (each 1H, br s, H-22)], one methoxy group [δ 3.84 (3H, s, OCH_3)], and six methyls [δ 1.85, 1.75, 1.48, 1.47, 1.45, 1.12, (each 3H, s)]. The ^{13}C NMR spectrum of **1** showed 26 signals. The evidence mentioned above and 11 unsaturated degrees from the molecular formula suggested that compound **1** possessed four rings.

Table 1. ^{13}C NMR Data of Compounds **1**−**4** (**1**, **3**, and **4** in $CDCl_3$; **2** in acetone-d_6, 150 MHz)[a]

no.	1	2	3	4
1	34.3	26.6	29.1	33.4
2	32.6	32.6	32.6	39.9
3	213.8	210.9	213.9	212.9
4	47.9	52.1	47.9	46.7
5	137.2	87.5	131.9	62.9
6	139.0	201.1	138.7	206.8
7	197.9	200.5	197.4	85.3
8	45.8	58.9	52.9	49.7
9	52.9	83.5	77.9	58.2
10	38.2	47.4	43.2	42.9
11	29.1	34.8	35.1	28.8
12	143.0	139.5	140.4	143.6
13	50.5	48.8	49.3	52.0
14	49.1	43.6	44.9	56.8
15	166.9	167.0	169.3	169.1
16	85.9	85.5	77.4	86.2
17	201.3	201.9	206.5	200.4
18	20.9	20.5	21.2	21.9
19	23.7	22.8	23.6	24.0
20	16.5	16.3	18.6	13.0
21	16.8	20.3	19.9	16.4
22	112.1	115.9	116.6	112.0
23	23.5	24.0	22.8	23.6
24	22.0	20.9	14.6	22.2
25	168.4	167.9		168.3
1′	53.7	53.1		53.9

[a] Assignments based on HSQC and HMBC.

The NMR data of compound **1** were very similar to those of terretonin (**6**), except for an additional ^{1}H NMR signal at δ 1.55 (dd, J = 12.8, 2.1 Hz, H-9) and its corresponding ^{13}C NMR signal at δ 52.9 for C-9 in compound **1** in place of a ^{13}C NMR signal at δ 77.6 for C-9 as in compound **6**. The HMBC correlation of H-9 with C-20 (16.5), C-21 (16.8), C-12

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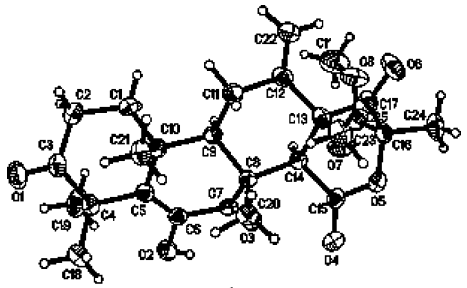
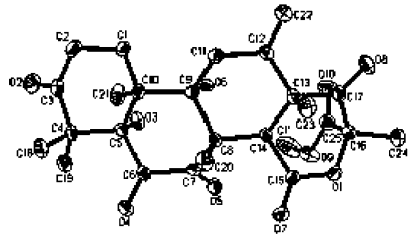
Table 2. ^{1}H NMR Data of Compounds **1**−**4** (**1**, **3**, and **4** in $CDCl_3$; **2** in acetone-d_6, 600 MHz)[a]

no.	**1** δ (m, J = Hz)	**2** δ (m, J = Hz)	**3** δ (m, J = Hz)	**4** δ (m, J = Hz)
1	1.72 dd 13.8, 10.6	1.91 ddd 16.1, 7.6, 2.4	1.80 dd 18.4, 8.5	1.63 td, 13.3, 4.8
	2.19 dd 13.6, 9.1	2.61 ddd 18.6, 12.6, 6.5	2.40 ddd 18.6, 11.3, 8.6	2.20 ddd, 13.2, 6.3, 2.5
2	2.56 dd 14.1, 10.6	2.36 ddd 16.2, 6.0, 2.5	2.54 ddd 19.3, 11.3, 8.9	2.31 ddd 15.1, 4.6, 2.5
	2.70 dd 13.8, 9.0	2.86 ddd 16.2, 11.6, 7.5	2.73 dd 19.1, 8.6	2.80 td, 14.4, 6.3
5				2.46 s
7				3.91 d, 2.6
9	1.55 dd, 12.8, 2.4			1.47 dd, 11.3, 1.4
11	2.34 dd 13.8, 2.4	2.52 d 14.4	2.28 d 15.0	2.36 dd 13.8, 1.4
	2.51 dd 13.8, 12.8	3.45 d 14.4	3.00 d 15.0	2.52 t 13.3
14	2.84 s	4.02 s	3.84 s	2.96 s
16			5.07 q 6.6	
18	1.47 s	1.50 s	1.46 s	1.52 s
19	1.48 s	1.15 s	1.46 s	1.10 s
20	1.85 s	1.85 s	1.97 s	1.42 s
21	1.12 s	1.63 s	1.23 s	1.17 s
22	5.17 br s	5.44 br s	5.39 br s	5.11 br s
	5.00 br s	5.04 br s	5.06 br s	4.99 br s
23	1.45 s	1.44 s	1.42 s	1.41 s
24	1.75 s	1.64 s	1.50 d 6.6	1.73 s
1′	3.84 s	3.77 s		3.87 s

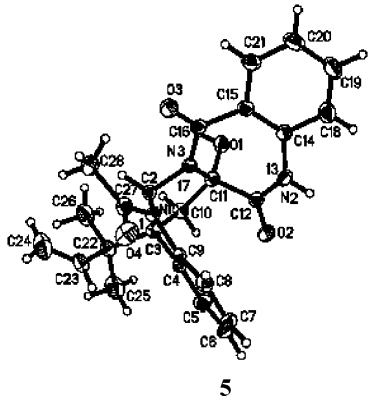
[a] Assignments based on HSQC and HMBC.



1



2



5

Figure 1. ORTEP diagram of compounds **1**, **2**, and **5**.

(143.0), C-11 (29.1), and C-10 (38.2) confirmed that compound **1** lacks the 9-OH found in compound **6**.

The relative stereochemistry of **1** was assigned on the basis of NOESY cross signals: H-14/H-9 and H-1′, and H-20/H-21 and H-23. X-ray crystallographic analysis confirmed the structure of **1** (Figure 1).

Compound **2** was obtained as colorless cubic crystals. Its molecular formula $C_{26}H_{32}O_{10}$ was provided by the HRESIMS quasi-molecular ion peak at m/z 527.1904 $[M + Na]^+$. The ^{1}H NMR (Table 2) spectrum suggested a vinylidine moiety [δ 5.17 and 5.00 (each 1H, br s, H-22)], one methoxy group [δ 3.84 (3H, s, OCH_3)], and six methyl groups [δ 1.85, 1.64, 1.63, 1.50, 1.44, 1.15, (each 3H, s)]. Four ketone carbonyls, two ester carbonyls, two double-bond carbons, and three oxygenated quaternary carbons were recognized among the 26 signals in the ^{13}C NMR spectrum. The structure of **2** was determined from HSQC and HMBC experiments. The stereochemistry of compound **2** was partly determined by NOESY cross-peaks: 5-OH (6.14)/9-OH (6.98), H-14/H-1′, and H-20/H-21 and H-23, and later confirmed by X-ray crystallographic analysis (Figure 1).

Compound **3** was obtained as colorless needles with a molecular formula of $C_{24}H_{30}O_7$ (HRESIMS). The ^{1}H NMR spectrum (Table 2) exhibited signals for a vinylidine moiety [δ 5.39 and 5.06 (each 1H, br s, H-22)], one methine proton (δ 5.07, q, J = 6.6 Hz, H-16), and six methyl groups [δ1.97, 1.46, 1.46, 1.42, 1.23, (each 3H, s), 1.50 (3H, d, J = 6.6 Hz, H-24)]. Three ketone carbonyls, one ester carbonyl, four double-bound carbon atoms, and two oxygenated carbon atoms were recognized among the 24 signals in the ^{13}C NMR spectrum. The structure of **3** was elucidated by HSQC and HMBC experiments. The stereochemistry of **3** was determined on the basis of NOESY correlations.

Compound **4** was obtained as colorless needles. Its molecular formula $C_{26}H_{34}O_8$ was provided by the HRESIMS quasi-molecular ion peak at m/z 497.2137 $[M + Na]^+$, suggesting 10 degrees of unsaturation. The ^{1}H NMR spectrum showed signals for a vinylidine moiety [δ_H 5.11 and 4.99 (each 1H, br s, H-22)], one methine proton (δ_H 3.91, d, J = 2.6 Hz, H-7), one methoxy group [δ_H 3.87 (3H, s, OCH_3)], and six methyl groups [δ_H 1.73, 1.52, 1.42, 1.41, 1.17, 1.10, (each 3H, s)]. The ^{13}C NMR spectrum revealed three ketone carbons, two ester carbonyls, two double-bond carbons, one oxygenated tertiary carbon, and one oxygenated quaternary carbon. The structure of **4** was established on the basis of HSQC and HMBC experiments. The relative stereochemistry of **4** was determined by the NOESY cross signals.

Compound **5** was obtained as colorless cubic crystals. The IR peaks at ν_{max} 3273, 1691, and 1647 cm^{-1} and the ^{13}C NMR signals at δ 170.0, 168.7, and 166.4 indicated the presence of amides. The ^{1}H NMR signals at δ 5.07 (1H, d, J = 10.6 Hz), 5.08 (1H, d, J = 17.6 Hz), and 5.87 (1H, dd,

J = 17.6, 10.6 Hz) and the HMBC correlations of methyls at δ 0.86 and 1.08 (each 3H, s) with the C atoms at δ 57.6, 40.7, and 144.1 suggested the moiety $-C(CH_3)_2CH{=}CH_2$. The ^{1}H NMR signals between δ 6.90 and 7.82 indicated the presence of two ortho-substituted phenyl rings. The NMR data of compound **5** were very similar to that of LL-S490β isolated from an unidentified *Aspergillus* species. [9] Comparison of the ^{13}C NMR spectrum of **5** with that of LL-S490β indicated that compound **5** contained one more oxygenated quaternary carbon at δ 88.3 and one less methine carbon at δ 58.0. The molecular formula $C_{25}H_{25}N_3O_4$ from the ion peak at *m/z* 430.1760 $[M - H]^-$ in the HRESIMS spectrum confirmed this conclusion. In the HMBC experiment, H-13 (δ 10.1) and H-10 (δ 2.41 and 3.57, each 1H, d, J = 13.6 Hz) correlated with C-11 (δ 88.3). Thus, the oxygenated C atom could be assigned only to C-11. The structure of compound **5** was subsequently confirmed by X-ray crystallographic analysis (Figure 1).

Compounds **1**, **6**, and territrem A exhibited no cytotoxicity against human breast cancer (Bre04), human lung cancer (Lu04), or human neuroma (N04) cell lines (GI_{50} > 100 μg/mL) and no inhibitory activity against α-amylase, sucrase, or maltase (IC_{50} > 100 μg/mL) in vitro.

Experimental Section

General Experimental Procedures. Melting points were determined on an X-6 precise melting point apparatus (Beijing Fukai Science and Technology Development Limited Company) and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. UV spectra and IR spectra were carried out on a Perkin-Elmer Lambda 35 UV/vis spectrometer and a Perkin-Elmer Spectrum One FT-IR spectrometer, respectively. NMR spectra were performed on a Bruker Avance 600 spectrometer. Electrospray ionization mass spectra (ESIMS) were acquired on a Finnigan LCQ^{DECA} mass spectrometer. High-resolution electrospray ionization mass spectra (HRESIMS) were obtained on a BioTOF-Q mass spectrometer. X-ray crystallographic data of compounds **1** and **5** were collected on a Bruker SMART-1000 CCD diffractometer and **2** on a Siemens P4 four-circle diffractometer. Silica gel (200−300 mesh) for column chromatography (CC) and silica gel GF254 (10−40 μm) for TLC were obtained from Qingdao Haiyang Chemical Company, China. All solvents including petroleum ether (60−90 °C) were distilled prior to use.

Microorganism and Fermentation. *A. terreus* (As 3.3955) was purchased from Perkin Institute of Microbiology of the Chinese Academy of Sciences. It was maintained on a potato dextrose agar slant (PDA) at °C and was stocked in Chengdu Institute of Biology of the Chinese Academy of Sciences. Seed culture medium was comprised of dextrose (20 g/L), yeast extract (1 g/L), KH_2PO_4 (3 g/L), $MgSO_4{\cdot}7H_2O$ (1.5 g/L), and potato extract prepared by extracting 200 g of potato with 1 L boiling water for 20 min. The pH of the medium was adjusted to 6.0 with 1 mol/L NaOH (aq). Solid culture medium was comprised of rice and 0.1% peptone. The sterilization was carried out at 121 °C under 15 psi for 30 min.

The fresh mycelium grown on a PDA slant at 28 °C for 3 days was inoculated into 500 mL flasks containing 100 mL of sterilized seed medium. Flasks with inoculated medium were placed in a rotary shaker at 28 °C and incubated at 180 rpm for 2 days. The seed culture was inoculated into a sterilized solid medium for further fermentation at 28 °C for 20 days.

Extraction and Isolation. The fermented solid medium (5 kg) was soaked with ethyl acetate (5 L × 3, 2 days for each time) at room temperature. The solvent was evaporated in vacuo to afford a residue (80 g). The residue was separated on a silica gel column (770 g, 160−200 mesh, ϕ 150 mm × 330 mm), eluted with petroleum ether−acetone (40:1, 30:1, 20:1, 10:1, 5:1, 2:1, 1:1, 1:2, each 5000 mL), to yield six fractions: A (15.0 g), B (7.0 g), C (10.0 g), D (25.0 g), E (5.0 g), and F (5.0 g). Compounds **1** (150 mg) and **6** (110 mg) were obtained by crystallizing fractions B and C from acetone, respectively. The separation of fraction B by silica gel CC (70 g, 200−300 mesh, ϕ 42 mm × 190 mm) eluted with petroleum ether−acetone (10:1, 8:1, 6:1, each 300 mL) yielded **1** (180 mg) and **4** (150 mg). CC of fraction D (500 g, 200−300 mesh, ϕ 76 mm × 230 mm) eluted with petroleum ether−ethyl acetate (5:1, 4:1, 3:1, 2:1, 1:1, 1:2, each 3000 mL) afforded four subfractions: D1−D4. Part of D1 (2.0 g) was separated by CC (60 g, 200−300 mesh, ϕ 31 mm × 160 mm) eluted with petroleum ether−acetone (3:1, 400 mL) to butyrolactone A (1.6 g). Territrem A (75 mg) and territrem B (105 mg) were obtained by crystallizing D2 from petroleum ether−acetone (1:1) and D3 from acetone, respectively. The mother liquid (1.2 g) of territrem B was subjected to CC (62 g, 200−300 mesh, ϕ 23 mm × 310 mm) with petroleum ether−acetone (35:1, 25:1, 20:1, 15:1, 10:1, 5:1, 2:1, each 400 mL) to give **2** (10 mg) and **3** (15 mg). D4 (220 mg) was further separated by CC (22 g, 200−300 mesh, ϕ 16 mm × 220 mm) eluted with petroleum ether−acetone (1.5: 1, 500 mL) to give compound **5** (30 mg). Fraction E was separated by CC (60 g, 200−300 mesh, ϕ 42 mm × 170 mm) with petroleum ether−acetone (3:1, 2:1, 1:1, each 1000 mL) to give butyrolactone B (120 mg).

Terretonin A (1): colorless cubic crystals (acetone), mp 232−233 °C; $[\alpha]_D^{20}$ −115.7°, $[\alpha]_{365}^{20}$ −516.4°, $[\alpha]_{436}^{20}$ −253.6°, $[\alpha]_{546}^{20}$ −142.9°, $[\alpha]_{578}^{20}$ −122.1° (*c* 0.14, $CHCl_3$); UV (MeOH) λ_{max} nm (log ϵ) 277 (4.06), 219 (2.01); IR (KBr) ν_{max} cm^{-1} 3386, 3001, 2970, 2934, 2871, 1778, 1755, 1735, 1708, 1681, 1634, 1455, 1257, 1106, 934; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; HRESIMS *m/z* 471.2025 $[M - H]^-$ (calc for $C_{26}H_{31}O_8$, 471.2013).

Terretonin B (2): colorless cubic crystals (acetone), mp 197−198 °C; $[\alpha]_D^{20}$ +10.0°, $[\alpha]_{365}^{20}$ −1138.0°, $[\alpha]_{436}^{20}$ +212.0°, $[\alpha]_{546}^{20}$ +24.0°, $[\alpha]_{578}^{20}$ +16.0° (*c* 0.10, acetone); UV (MeOH) λ_{max} nm (log ϵ) 288 (3.77); IR (KBr) ν_{max} 3338, 3004, 2948, 1779, 1749, 1732, 1680, 1645, 1441, 1266, 1114, 914 cm^{-1}; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; HRESIMS (positive mode) *m/z* 527.1904 $[M + Na]^+$ (calc for $C_{26}H_{32}NaO_{10}$, 527.1888).

Terretonin C (3): colorless needles (petroleum ether), mp 228−229 °C; $[\alpha]_D^{20}$ −263.3°, $[\alpha]_{365}^{20}$ −1510.0°, $[\alpha]_{436}^{20}$ −654.2°, $[\alpha]_{546}^{20}$ +24.0°, $[\alpha]_{578}^{20}$ +16.0° (*c* 0.10, acetone); UV (MeOH) λ_{max} nm (log °) 277 (4.13), 202 (3.90); IR (KBr) ν_{max} cm^{-1} 3609, 3490, 3379, 2980, 2939, 1759, 1735, 1695, 1673, 1643, 1631, 1473, 1187, 933; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; HRESIMS (positive mode) *m/z* 453.1901 $[M + Na]^+$ (calc for $C_{24}H_{30}NaO_7$, 453.1884).

Terretonin D (4): colorless needles (acetone), mp 157−158 °C; $[\alpha]_D^{20}$ −43.3°, $[\alpha]_{365}^{20}$ −283.3°, $[\alpha]_{436}^{20}$ −109.2°, $[\alpha]_{546}^{20}$ −50°, $[\alpha]_{578}^{20}$ −41.7° (*c* 0.12, $CHCl_3$); UV (MeOH) λ_{max} nm (log ϵ) 280 (3.47), 218 (4.36); IR (KBr) ν_{max} cm^{-1} 3456, 2980, 2943, 2873, 1781, 1733, 1712, 1673, 1641, 1446, 1267, 1117, 929; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; HRESIMS (positive mode) *m/z* 497.2137 $[M + Na]^+$ (calc for $C_{26}H_{34}NaO_8$, 497.2146).

Asterrelenin (5): colorless cubic crystals (acetone−methanol−H_2O, 3:1:1), mp 199−200 °C; $[\alpha]_D^{20}$ +206.0° $[\alpha]_{365}^{20}$ +852.0°, $[\alpha]_{436}^{20}$ +472.0°, $[\alpha]_{546}^{20}$ +254.0°, $[\alpha]_{578}^{20}$ +221.0° (*c* 0.10, CH_3OH); UV (MeOH) λ_{max} nm (log ϵ) 284 (4.25), 228 (3.29); IR (KBr) ν_{max}cm^{-1} 3273, 2975, 2928, 1691, 1647, 1484, 1462, 1379, 1161, 756; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.82 (1H, dd, J = 7.8, 1.4 Hz, H-5), 7.61 (1H, dd, J = 6.7, 1.1 Hz, H-7), 7.41 (1H, td, J = 7.6, 1.4 Hz, H-7), 7.37 (1H, dd, J = 7.6, 0.9 Hz, H-21), 7.16 (1H, td, J = 8.2, 0.9 Hz, H-19), 7.11 (1H, td, J = 7.4, 0.9 Hz, H-20), 7.05 (1H, td, J = 7.6, 0.9 Hz, H-6), 6.90 (1H, dd, J = 8.0, 1.3 Hz, H-18), 6.18 (1H, s, H-2), 5.87 (1H, dd, J = 17.6, 10.6 Hz, H-23), 5.09 (1H, d, J = 17.6 Hz, H-24a), 5.07 (1H, d, J = 10.6 Hz, H-24b), 3.57 (1H, d, J = 13.6 Hz, H-10a), 2.59 (3H, s, H-28), 2.41 (1H, d, J = 13.6 Hz, H-10b), 1.08 (3H, s, H-25), 0.86 (3H, s, H-26); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.0 (C-27), 168.7 (C-12), 166.4 (C-16), 144.1 (C-23), 142.0 (C-14), 137.3 (C-9), 133.1 (C-7), 133.1 (C-4), 130.6 (C-5), 128.3 (C-19), 127.5 (C-21), 124.9 (C-15), 123.7 (C-6), 123.3 (C-20), 120.3 (C-18), 118.5 (C-8), 114.3 (C-24), 88.3 (C-11), 81.6 (C-2), 57.6 (C-3), 40.5 (C-10), 40.5 (C-22), 23.8 (C-28), 23.2 (C-26), 22.7 (C-25); HRESIMS (negative mode) *m/z* 430.1760 $[M - H]^-$ (calc for $C_{25}H_{25}N_3O_4$, 430.1761).

X-ray Crystal Data of 1.[10] A colorless cubic crystal suitable for X-ray crystallographic analysis was obtained from acetone. Crystal data: $C_{26}H_{32}O_8$; M_r = 472.52; orthorhombic, space group $P2_12_12_1$, a = 8.6564(10) Å, b = 8.9699(10) Å, c = 15.7331(18) Å, $\alpha = \gamma = 90°$, $\beta = 91.5°$, V = 1221.2(2) Å^3, Z = 2, D_{calc} = 1.285 g/cm^3, λ = 0.71073 Å, μ(Mo Kα) = 0.095 mm^{-1}, $F(000)$ = 504, T = 293(2) K. Of the 8306 reflections that were collected, 3101 were unique (R_{int} = 0.0297). The structure was solved by direct methods with SHELXL-97 and refined by full-matrix least-squares on F^2. Final refinement: data/restraints/parameters = 3101/2/317; R_1 = 0.0491 (all data), wR_2 = 0.0999 (all data). Absolute structure parameter = 0(10) and GOF = 0.801. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.206 and −0.160 e$^-$/Å^3, respectively.

X-ray Crystal Data of 2.[10] A colorless cubic crystal suitable for X-ray crystallographic analysis was obtained from ethyl acetate. Crystal data: $C_{27}H_{36}O_{11}$ (including a molecular of methanol); M_r = 536.56; orthorhombic, space group $P2_12_12_1$, a = 9.582(1) Å, b = 10.553(2) Å, c = 26.621(5) Å, $\alpha = \gamma = \beta = 90°$, V = 2692.0(7) Å^3, Z = 4, D_{calc} = 1.324 Mg/m^3, λ = 0.71073 Å, μ(Mo Kα) = 0.103 mm^{-1}, $F(000)$ = 1144, T = 300(2) K. Of the 3833 reflections that were collected, 3534 were unique (R_{int} = 0.0138). The structure was solved by direct methods with SHELXS97 and refined by full-matrix least-squares on F^2. Final refinement: data/restraints/parameters = 3534/0/355; R_1 = 0.0791 (all data), wR_2 = 0.0808 (all data). Absolute structure parameter = 0(10) and GOF = 0.858. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.206 and −0.160 e$^-$/Å^3, respectively.

X-ray Crystal Data of 5.[10] A colorless cubic crystal was obtained from acetone−methanol−H_2O (3:1:1). Crystal data: $C_{26}H_{29}N_3O_5$ (including a molecule of methanol); M_r = 463.52; orthorhombic, space group $P2_12_12_1$, a = 8.9385(8) Å, b = 13.2286(12) Å, c = 19.7927(18) Å, $\alpha = \beta = \gamma = 90°$, V = 2340.4(4) Å^3, Z = 4, D_{calc} = 1.316 g/cm^3, λ = 0.71073 Å, μ(Mo Kα) = 0.092 mm^{-1}, $F(000)$ = 984, T = 293(2) K. Of the 8306 reflections that were collected, 3194 were unique (R_{int} = 0.0600). The structure was solved by direct methods with SHELXL-97 and refined by full-matrix least-squares on F^2. Final refinement: data/restraints/parameters = 3194/4/321; R_1 = 0.0488 (all data), wR_2 = 0.0791 (all data). Absolute structure parameter = 0(10) and GOF = 0.907. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.194 and −0.139 e$^-$/Å^3, respectively.

Supporting Information Available: HMBC and NOESY correlation figures of compounds **1**−**5** and key crystal information for compounds **1**, **2**, and **5** are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(10) Crystallographic data (including structure factors) for compounds **1** (CCDC260073), **2** (CCDC271951), and **5** (CCDC260072) reported in this paper have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, CB2 1EZ, UK [fax: +44-0-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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