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Thelephantins I–N: *p*-terphenyl derivatives from the inedible mushroom *Hydnellum caeruleum*

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Abstract

Phytochemical investigation of the methanolic extract of the fruiting bodies of the inedible mushroom *Hydnellum caeruleum* resulted in the isolation of six *p*-terphenyl derivatives named thelephantins I–N (**1**–**6**), together with a known compound, dihydroaurantiacin dibenzoate (**7**). These structures were determined by high-resolution MS, 2D NMR, IR and UV spectroscopic analysis, and by the chemical reactions.

Keywords: *Hydnellum caeruleum*; Thelephoraceae; Fungi; Thelephantins; 3-Pyridinecarboxylate

1. Introduction

The mushrooms belonging to the Thelephoraceae family have been shown to be a rich source of *p*-terphenyl compounds. Sullivan et al. (1967) reported the isolation of atromentin, aurantiacin, dihydroaurantiacin dibenzoate, polyporic acid and thelephoric acid from *Hydnellum* genus. Recently, ganbajunins A–G from *Thelephora ganbajun* (Hu et al., 2001a,b) and thelephorin A from *Thelephora vialis* (Tsukamoto et al., 2002) were reported. We also reported the isolation of curtisians E–Q from the Badisiomycete fungi, *Paxillus curtisii* (Quang et al., 2003a,b,c) and thelephantins A–H (Quang et al., 2003d,e) from *Thelephora aurantiotincta*. In the course of our investigation of the biologically active substances from the inedible mushrooms, we investigated the chemical constituents of *Hydnellum caeruleum* and isolated six new *p*-terphenyl derivatives named thelephantins I–N (**1**–**6**) together with a known *p*-terphenyl, dihydroaurantiacin dibenzoate (**7**). We wish to report here on their isolation and structural elucidation.

2. Results and discussion

The methanolic extract of the fruit bodies of *H. caeruleum* was subjected to Sephadex LH-20 and SiO_2 column chromatography, and then prep. HPLC to afford thelephantins I–N (**1**–**6**), together with a known compound dihydroaurantiacin dibenzoate (**7**) (Sullivan et al., 1967).

The molecular formula of thelephantin I (**1**) was determined to be $C_{26}H_{18}O_7$ by HR-FABMS. The FT-IR, UV and ^{13}C NMR spectra of compound **1** indicated the presence of a hydroxyl (3376 cm^{-1}) group and a *para*-quinone (1661 cm^{-1}, λ_{max} 397 nm, δ_C 182.2 and 184.3). The ^1H NMR spectrum of **1** (Table 1) indicated the presence of a methoxyl group and a benzoyl group and its spectrum was very similar to that of 2′-*O*-methylatromentin (**8**) (Hu et al., 2001a), except for the signals of a benzoyl group suggesting that compound **1** is a *p*-terphenyl derivative. The positions of the benzoyl and methoxyl groups were located at 2′ and 5′, respectively,

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Table 1
^{1}H-NMR spectral data for compounds **1–6** (600 MHz, CD_3OD)

H	1	2	3	4	5	6
2, 6	7.27 *d* 8.8	7.27 *d* 8.8	7.26 *d* 8.8	7.22 *d* 8.8	7.26 *d* 8.8	7.26 *d* 8.8
3, 5	6.79 *d* 8.8	6.75 *d* 8.8	6.74 *d* 8.8	6.75 *d* 8.8	6.75 *d* 8.8	6.75 *d* 8.8
2″	7.21 *d* 8.8	7.27 *d* 8.8	7.30 *d* 8.8	7.24 *d* 8.8		7.26 *d* 8.8
3″	6.83 *d* 8.8	6.75 *d* 8.8	6.77 *d* 8.8	6.65 *d* 8.8	7.09 *s*	6.75 *d* 8.8
5″	6.83 *d* 8.8	6.75 *d* 8.8	6.62 *d* 8.8	6.65 *d* 8.8		6.75 *d* 8.8
6″	7.21 *d* 8.8	7.27 *d* 8.8	7.21 *d* 8.8	7.24 *d* 8.8	7.02 *s*	7.26 *d* 8.8
3a, 7a	8.01 *d* 8.2	7.74 *dd* 1.4, 8.5	7.76 *d* 8.5	7.79 *d* 8.2	7.81 *d* 8.5	7.77 *dd* 1.1, 8.6
4a, 6a	7.49 *dd* 7.4, 8.2	7.26 *t* 8.5	7.28 (overlap)	7.28 *t* 8.2	7.32 *dd* 7.7, 8.5	7.29 *t* 7.7
5a	7.65 *t* 7.4	7.43 *t* 8.5	7.44 *t* 7.7	7.47 *t* 8.2	7.49 *t* 7.7	7.46 *t* 7.7
3b			8.01 *d* 8.5	7.79 *d* 8.2		
4b, 6b			7.47 *t* 8.2	7.28 *t* 8.2		
5b			7.59 *m*	7.47 *t* 8.2		
7b			7.97 *d* 8.5	7.79 *d* 8.2		
1c	3.81 *s*					
3c		7.74 *d* 8.5	7.76 *d* 8.5	7.97 *d* 8.5	8.13 *dd* 1.4, 8.2	8.11 *d* 8.0
4c		7.26 *t* 8.5	7.28 (overlap)	7.49 *t* 8.5	7.47 *dd* 7.7, 8.2	7.36 *dd* 4.7, 8.0
5c		7.43 *t* 8.5	7.44 *t* 7.7	7.64 *t* 8.5	7.62 *t* 7.7	8.58 *brd* 4.7
6c		7.26 *t* 8.5	7.28 (overlap)	7.49 *t* 8.5	7.47 *dd* 7.7, 8.2	
7c		7.74 *d* 8.5	7.76 *d* 8.5	7.97 *d* 8.5	8.13 *dd* 1.4, 8.2	8.84 *brs*
2d				1.84 *s*		

by the NOE correlations between (1) H-3a/H-2 and H-3; (2) CH_3O-(H-1c)/H-5″ and H-6″ in its NOESY spectrum. In addition, the ^{13}C NMR and UV spectral data of **1** were in good agreement with those of 2′-*O*-methylatromentin (Hu et al., 2001a). Thus, thelephantin I (**1**) was determined to be 4,4″-dihydroxy-2′-benzoyloxy-5′-methoxy [1,1′:4′,1″-terphenyl]-3′,6′-dione as shown.

A molecular formula of $C_{32}H_{22}O_8$ was determined for thelephantin J (**2**) from the molecular ion peak at *m*/*z* 534.1341 $[M]^+$ (calc. for $C_{32}H_{22}O_8$ 534.1315) obtained by HR-FABMS. The ^{1}H NMR spectrum (Table 1) of compound **2** showed the signals of eight aromatic protons and two benzoyl groups. The ^{13}C NMR spectrum (Table 2) of **2** displayed the resonances of phenolic carbons (δ_C 142.7, 158.0) and carbonyl ester (δ_C 166.4). The ^{1}H and ^{13}C NMR spectral data of **2** were very similar to those of thelephorin A (Tsukamoto et al., 2002) and thelephantins A–H (Quang et al., 2003d,e) suggesting that compound **2** is a 2′,5′-dibenzoyl-*p*-terphenyl derivative. In addition, the signals observed in the ^{1}H and ^{13}C NMR spectrum of **2** (Tables 1 and 2) showed exact overlapping along the terphenyl bond axis, suggesting that this compound has symmetrical structure (Yun et al., 2000; Quang et al., 2003a). Further, the location of two benzoyl groups was deduced by oxidative treatment. Compound **2** was oxidized by di-ammonium cerium (IV) nitrate to give quinone derivative **9** (UV λ_{max} 495 nm and IR 1671 cm^{-1}) (Chart 1) indicating that **2** had a hydroquinone moiety. The presence of quinone group was also confirmed by observation of the molecular ion peak at *m*/*z* 555.1039 ($C_{32}H_{20}O_8Na$) in HR-FABMS, indicating the loss of two molecular weights from the original compound (**2**). The ^{13}C NMR spectral data of **9** resembled those of **2** except for the presence of

Table 2
^{13}C-NMR spectral data for compound **1–6** (150 MHz, CD_3OD)

C	1	2	3	4	5	6
1	120.8	124.9	124.9	123.2	125.1	124.8
2.6	132.9	132.6	132.6	131.9	132.9	132.6
3.5	115.9	116.0	116.0	116.1	115.9	116.0
4	159.9	158.0	158.0	158.8	157.9	158.2
1′	129.4	124.1	124.1	131.8	122.4	124.1
2′	148.3	132.6	135.0	140.9	137.5	134.9
3′	184.3	142.7	134.8	140.9	144.5	142.9
4′	129.2	124.1	124.1	131.8	119.7	124.1
5′	156.3	132.6	135.0	140.9	139.2	134.6
6′	182.2	142.7	142.7	140.9	142.7	142.9
1″	122.0	124.9	124.9	123.2	115.0	124.8
2″	133.3	132.6	132.7	131.9	152.6	132.6
3″	115.7	116.0	116.1	116.1	99.4	116.0
4″	159.2	158.0	158.3	158.8	148.3	158.1
5″	115.7	116.0	115.9	116.1	143.8	116.0
6″	133.3	132.6	132.0	131.9	107.4	132.6
1a	165.7	166.4	166.4	165.4	166.3	166.3
2a	134.8	130.1	130.8	129.4	129.8	129.9
3a, 7a	131.3	130.7	130.7	130.9	130.8	130.7
4a, 6a	129.9	129.4	129.5	129.6	129.6	129.6
5a	135.4	134.6	134.6	135.0	134.7	134.8
1b			166.3	165.4	165.9	
2b			129.8	129.4	130.0	
3b			130.5	130.9	131.2	
4b, 6b			129.5	129.6	130.0	
5b			134.2	135.0	135.2	
7b			131.1	130.9	131.2	
1c	61.8	166.4	166.4	165.3		164.5
2c		130.1	130.8	129.4		126.7
3c		130.7	130.7	131.0		139.0
4c		129.4	129.5	129.9		125.2
5c		134.6	134.6	135.3		154.4
6c		129.4	129.5	129.9		
7c		130.7	130.7	131.0		151.1
1d				169.6		
2d				20.0		

signal at 176.9 ppm in place of the phenolic carbon at 142.7 ppm and absorption maximum at 495 nm in its UV spectrum suggesting the presence of a *para*-benzoquinone moiety in **9** (Quang et al., 2003b). In addition, no bathochromic shift of absorption maximum at 495 nm in its UV spectrum was observed when one and then ten drops of a H_3BO_3 solution (1% in water) was added, indicating that compound **9** was not an *ortho*-benzoquinone. Consequently, thelephantin J (**2**) was found to be 3′,4,4″,6′-tetrahydroxy-2′,5′-dibenzoyloxy [1,1′:4′,1″-terphenyl] as depicted in Chart 1.

Thelephantin K (**3**) was shown to have a molecular formula of $C_{39}H_{26}O_9$ by HR-FABMS. Inspection of its ^1H NMR spectral data suggested the presence of three benzoyl groups in **3**. Compound **3** also displayed 39 carbon signals in its ^{13}C NMR including three phenolic carbons, three carbonyl esters. By comparing its NMR spectral data with those of thelephantin J (**2**) indicated that compound (**3**) possessed three benzoyl groups at the central aromatic ring. Thus, thelephantin K (**3**) was deduced to be 4,4″,6′-trihydroxy-2′,3′,5′-tribenzoyloxy [1,1′:4′,1″-terphenyl] as shown.

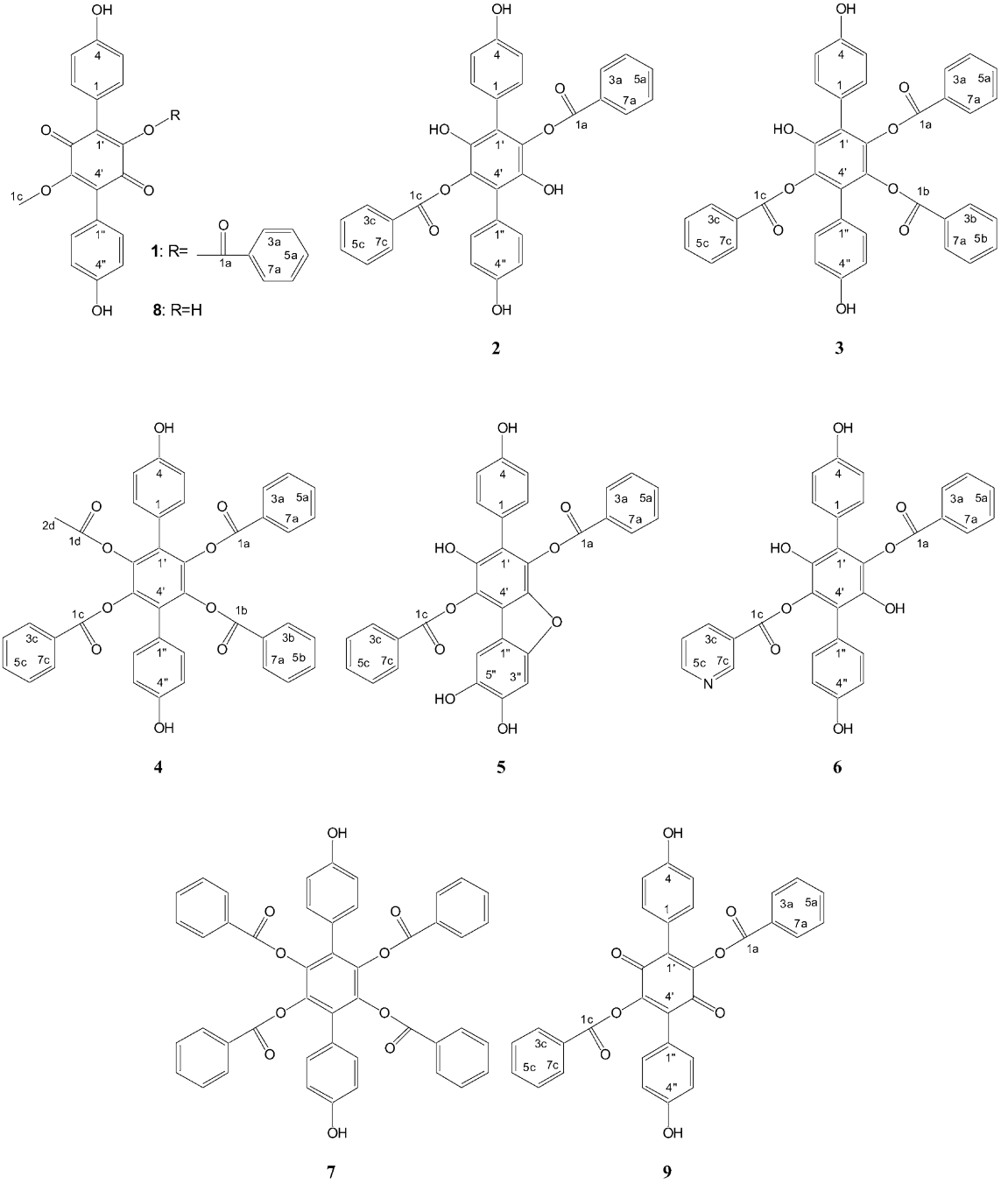

Chart 1. The structures of compounds **1**–**9**.

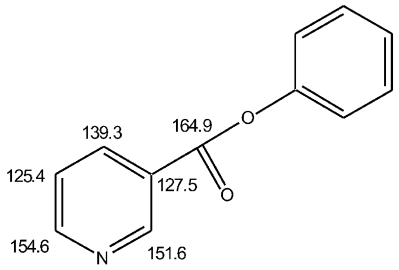

Chart 2. The important ^{13}C NMR data of phenyl 3-pyridinecarboxylate (CD_3OD).

HR-FABMS of thelephantin L (**4**) indicated the molecular formula $C_{41}H_{28}O_{10}$. The IR spectrum indicated the presence of a hydroxyl (3452 cm^{-1}), carbonyl ester (1748 cm^{-1}) and a benzene (1611, 1525 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra of compound **4** were very similar to those of thelephantin K (**3**) except for the presence of one acetyl group [δ_H 1.84 (s) and δ_C 169.6, 20.0]. Thus, the structure of thelephantin L (**4**) was deduced to be 4,4″-dihydroxy-2′,3′,5′-tribenzoyloxy-6′-acetyloxy [1,1′:4′,1″-terphenyl] as shown.

The molecular formula of thelephantin M (**5**) was found to be $C_{32}H_{20}O_9$ by HR-FABMS. The ^1H NMR spectrum (Table 1) of **5** showed the presence of fourteen aromatic and two singlet aromatic protons. The spectral data of compound **5** resembled those of thelephantin H (Quang et al., 2003e) suggesting that it was also a *p*-terphenyl derivative possessing a dibenzofuran unit due to the long-range correlations between (i) H-3″ and C-1″, C-2″, C-4″ and C-5″; (ii) H-6″ and C-4′, C-2″, C-4″ and C-5″, except for the notable difference in the NMR spectral data of two substitution groups at the central aromatic ring. Two substitution groups were determined to be benzoyl groups by its 2D NMR spectroscopy and located at C-2′ and C-5′ by the NOE correlations between (i) H-3a and H-6; (ii) H-3c and H-6″ in its NOESY spectrum. Based on the above discussion, thelephantin M (**5**) was found to be di[benzoic acid] 2,7,8-trihydroxy-3(-4-hydroxyphenyl)dibenzofuran-1,4-diyl ester as shown.

Thelephantin N (**6**) was obtained as grayish solid; its molecular formula was determined to be $C_{31}H_{21}O_8N$ by HR-FABMS indicated the presence of a nitrogen atom. The NMR spectral data (Tables 1 and 2) of **6** were very similar to those of thelephantin J (**2**) indicating that it was a *p*-terphenyl derivative with two substitution groups, one of which was a benzoyl group. The ^1H NMR spectral data of the other substitution group showed the presence of four aromatic proton signals, in which H-4c correlated to H-3c and H-5c in its ^1H–^1H COSY spectrum, and the signal of H-7c was shifted to the down field at δ_H 8.84 (br s). In addition, the ^{13}C NMR spectrum (Table 2) of this substitution group showed the presence of one carbonyl ester and five aromatic carbons. Thus, the second substitution group at the central aromatic ring was determined to be 3-pyridinecarboxyl. It was further confirmed by comparison of the ^{13}C NMR spectral data of **6** with those of the commercially available phenyl 3-pyridinecarboxylate (Chart 2). The ^{13}C NMR signals of 3-pyridinecarboxyl partial structure of **6** were almost identical with those of phenyl 3-pyridinecarboxylate. Two substitutions groups at the central aromatic ring were determined to be at C-3′ and C-5′ by comparing its ^{13}C NMR spectral data to those of thelephantin J (**2**) and thelephantins A–H (Quang et al., 2003d,e). Thus, the structure of thelephantin N (**6**) was determined to be 3′,4,4″,6′-tetrahydroxy-2′-benzoyloxy-5′-(3-pyridinecarboxyl) [1,1′:4′,1″-terphenyl] as shown. This is the second report of a terphenyl compound possessing a nitrogen atom. Previously, sarcodonin, a *p*-terphenyl derivative with an N-oxide and a hydroxylamine, was reported from fruiting bodies of *Sarcodon leucopus* belonging to the same family Thelephoraceae (Corrada et al., 2000).

3. Experimental

3.1. General

NMR spectra were recorded on Varian Unity 600 (600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR) using CD_3OD unless otherwise stated. Chemical shifts are given with TMS (δ 0.00) used as internal standard (^1H-NMR) and δ 49.00 (ppm) from CD_3OD as a standard (^{13}C-NMR). IR spectra were measured on JASCO FT/IR-5300 spectrophotometer. UV spectra were obtained on a Shimadzu UV-1650PC in MeOH solution. Mass spectra including high-resolution FAB mass spectra were recorded on a JEOL JMS AX-500 spectrometer. Column chromatography was carried out on silica gel 60 (0.2–0.5 mm, and 0.04–0.063 mm, Merck) and Sephadex LH-20 (Amersham Pharmacia Biotech, $CHCl_3$–MeOH, 1:1). Preparative medium-pressure liquid chromatography (MPLC) was performed with a Work-21 pump (Lab-Quatec Co., Ltd) and carried out by Lobar column chromatography (Merck). HPLC was performed on a Shimadzu liquid chromatograph LC-10AS with RID-6A and SPD-10A detectors using a Waters 5C18-AR-II column. The spots on TLC were detected under UV 254 nm and by spraying with Godin reagent (Godin, 1954), followed by heating at 120 °C.

3.2. Material

Fruit bodies of *Hydnellum caeruleum* was collected in Yatugatake mountain, Shinshou, Nagano Prefecture, Japan in August 1998 and identified by M. Nukada at Kurashiki Sakuyo University, Kurashiki, Japan. The voucher specimen (K1998-1) has been deposited in Faculty of Food Culture, Kurashiki Sakuyo University, Kurashiki 710-0290 Japan.

3.3. Extraction and isolation

The dried fruit bodies of *H. caeruleum* (20 g) was extracted with MeOH followed by concentration in vacuo to give a residue (4.4 g) which was subjected to Sephadex LH-20 and then SiO_2 column chromatography using $CHCl_3$–MeOH (1:1) as eluent to give 6 fractions. Fraction 1 (23.8 mg) was further purified by preparative HPLC with a reversed phase RP-18 column, solvent system CH_3CN–H_2O (1:1) yielded compounds **1** (15.2 mg), **4** (2.2 mg). Fraction 2 (307.4 mg) was treated in the same manner as fraction 1 to give compounds **1** (21.2 mg), **4** (7.7 mg) and **7** (4.4 mg). Fraction 3 (92.8 mg) was treated in the same procedure to give sub-fractions 1 and 2, then purified by prep. HPLC with a DIOL column using EtOAc as solvent to afford compounds **1** (3.0 mg), **2** (5.9 mg) and **3** (25.7 mg). Fraction 4 (257.8 mg) gave compound **2** in pure state. Fraction 5 (56.1 mg) and 6 (49.0 mg) were treated in the same manner as fraction 1 to yield compounds **2** (7.7 mg), **5** (9.8 mg), and **6** (4.1 mg) from Fr. 5 and **2** (3.4 mg) and **5** (5.6 mg) from Fr. 6, respectively.

3.3.1. Thelephantin I (1)

Reddish orange solid; Positive FAB-MS: 443 $[M+H]^+$; HR-FABMS *m/z* 443.1086 ($C_{26}H_{19}O_7$, requires *m/z* 443.1131). UV λ_{max} nm (log ϵ): 241.5 (4.4), 248.5 (4.4), 397.0 (3.6). IR (KBr): 3376, 1740, 1661, 1606, 1513 cm^{-1}. ^1H and ^{13}C NMR (Tables 1 and 2).

3.3.2. Thelephantin J (2)

Grayish solid; Positive FAB-MS: 534 $[M]^+$; HR-FABMS *m/z* 534.1341 ($C_{32}H_{22}O_8$, requires *m/z* 534.1315). UV λ_{max} nm (log ϵ): 231.0 (4.5), 262.0 (4.2). IR (KBr): 3258, 1720, 1610, 1526 cm^{-1}. ^1H and ^{13}C NMR (Tables 1 and 2).

3.3.3. Thelephantin K (3)

Grayish solid; Positive FAB-MS: 639 $[M+H]^+$; HR-FABMS *m/z* 639.1656 ($C_{39}H_{27}O_9$, requires *m/z* 639.1655). UV λ_{max} nm (log ϵ): 231.4 (4.5), 260.8 (4.1). IR (KBr): 3447, 1745, 1611, 1526 cm^{-1}. ^1H and ^{13}C NMR (Tables 1 and 2).

3.3.4. Thelephantin L (4)

Grayish solid; Positive FAB-MS: 703 $[M+Na]^+$; HR-FABMS *m/z* 703.1555 ($C_{41}H_{28}O_{10}Na$, requires *m/z* 703.1580). UV λ_{max} nm (log ϵ): 232.0 (4.7), 267.2 (4.3). IR (KBr): 3452, 1748, 1611, 1525 cm^{-1}. ^1H and ^{13}C NMR (Tables 1 and 2).

3.3.5. Thelephantin M (5)

Yellow brown solid; Positive FAB-MS: 548 $[M]^+$; HR-FABMS *m/z* 548.1108 ($C_{32}H_{20}O_9$, requires *m/z* 548.1107). UV λ_{max} nm (log ϵ): 229.8 (4.6), 265.8 (4.2), 299.2 (4.0), 321.8 (4.1), 329.4 (4.1). IR (KBr): 3221, 1735, 1610, 1523 cm^{-1}. ^1H and ^{13}C NMR (Tables 1 and 2).

3.3.6. Thelephantin N (6)

Grayish solid; Positive FAB-MS: 536 $[M+H]^+$; HR-FABMS *m/z* 536.1373 ($C_{31}H_{22}O_8N$, requires *m/z* 536.1345). UV λ_{max} nm (log ϵ): 226.6 (4.2), 264.0 (4.2). IR (KBr): 3354, 1743, 1610, 1525 cm^{-1}. ^1H and ^{13}C NMR (Tables 1 and 2).

3.3.7. Oxidation of thelephantin J (9)

Thelephantin J (**2**) (20.0 mg) was oxidized by di-ammonium cerium (IV) nitrate (25 mg) in MeCN (2 ml) at 0–5 °C for 25 min. The reaction mixture was treated in the same manner as curtisian I (Quang et al., 2003b) to afford **9** (10.8 mg). UV (MeOH): λ_{max} (log ϵ) 237 (4.4), 495 (3.1); IR (KBr): 3349, 1737, 1671, 1610, 1515, 1452, 1239, 1176, 1108, 1024 cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 176.9 (C-3′, C-6′), 167.3 (C-1a, C-1c), 157.9 (C-4, C-4″), 149.0 (C-2′, C-5′), 132.9 (C-5a, C-5c), 131.1 (C-2, C-6, C-2″, C6″), 129.1 (C1′, C-4′), 129.3 (C-3a, C-7a, C-3c, C-7c), 128.6 (C-4a, C-6a, C-4c, C-6c), 120.0 (C1, C1″), 115.0 (C-3, C-5, C-3″, C-5″); FABMS *m/z* 555 $[M+Na]^+$; HR-FABMS *m/z* 555.1039 ($C_{32}H_{20}O_8Na$, 555.1056).

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