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Anthraquinones from *Hedyotis capitellata* ☆

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Abstract

Four new furanoanthraquinones, 2-hydroxymethyl-3,4-[2′-(1-hydroxy-1-methylethyl)-dihydrofurano]-8-hydroxyanthraquinone, 2-hydroxymethyl-3,4-[1′-hydroxy-2′-(1-hydroxy-1-methylethyl)-dihydrofurano]-8-hydroxyanthraquinone, 2-hydroxymethyl-3,4-[2′-1-hydroxy-1-methylethyl)-dihydrofurano]anthraquinone and 2-methyl-3,4-[2′-(1-hydroxy-1-methylethyl)-dihydrofurano] anthraquinone or capitellataquinone A–D and four known anthraquinones, rubiadin, anthragallol 2-methyl ether, alizarin 1-methyl ether and digiferruginol, together with scopoletin were isolated from the stems of *Hedyotis capitellata* Wall (Rubiaceae). Lucidin-3-*O*-β-glucoside was isolated from the roots of the plant. Characterization of the new compounds was carried out by extensive NMR studies using FGCOSY, FGHMQC, FGHMBC and DEPT-135 in addition to other spectroscopic methods.
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Keywords: *Hedyotis capitellata*; Rubiaceae; Furanoanthraquinone; Capitellataquinone A, B, C and D

1. Introduction

Several species of *Hedyotis* (family Rubiaceae) are used in traditional medicine in a number of Asian countries including Malaysia. Phytochemical studies on the genus have shown it to be chemically diverse, yielding among others, β-carboline alkaloids (Phuong et al., 1999; Peng et al., 1997) and flavonol glycosides (Kim

Abbreviations: CC, column chromatography; DEPT, distortion enhancement by polarization transfer; EIMS, electron impact mass spectra; EtOH, ethanol; FDMS, field desorption mass spectroscopy; FGCOSY, field gradient correlated spectroscopy; FGHMBC, field gradient heteronuclear multiple bond coherence; FGHMQC, field gradient heteronuclear multiple quantum coherence; FTIR, Fourier transform infrared; HRMS, high resolution mass spectroscopy; NMR, nuclear magnetic resonance; TLC, thin layer chromatography; UV–Vis, ultraviolet–visible spectroscopy; ID, internal diameter.

☆ Part 5 in the series "Studies on *Hedyotis* species"

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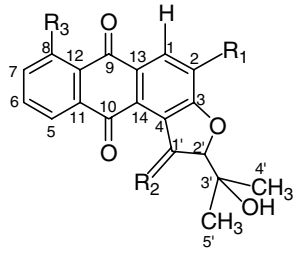
et al., 2001; Lu et al., 2000). Similarly, we have also previously reported the isolation of flavonoid glycosides, as well as anthraquinones and triterpenes from a number of *Hedyotis* species including *Hedyotis verticillata* (Hamzah et al., 1994), *Hedyotis dichotoma* (Hamzah et al., 1997), *Hedyotis herbacea* (Permana et al., 1999) and *Hedyotis diffusa* (Permana et al., 2003). In continuation of our studies on Malaysian *Hedyotis*, we now report the isolation of four new furanoanthraquinones (**1**–**4**), capitellataquinone A–D, with four known anthraquinones, rubiadin (**5**), anthragallol 2-methyl ether (**6**), alizarin 1-methyl ether (**7**) and digiferruginol (**8**) as well as scopoletin or 7-hydroxy-6-methoxycoumarin from the stems of *Hedyotis capitellata* Wall. An anthraquinone glycoside, lucidin-3-*O*-β-glucoside (**9**) was also isolated from the roots of the plant.

2. Results and discussion

The chloroform extract of the stems of *H. capitellata* was subjected to chromatographic separation and purification to yield four new furanoanthraquinones along with four known anthraquinones as well as scopoletin. The UV spectrum of compounds **1**–**4** (Fig. 1) with the common absorbance maxima at 245 and 280 nm were typical of an anthraquinone-type compound (Thomson, 1971). For compounds **1** and **2**, a maximum was also observed at 415 nm. For compounds **3** and **4**, this peak was not seen; instead, a maximum appeared at a shorter wavelength of 385 nm. The IR spectra of all four compounds also showed characteristic absorption bands for free hydroxyl in the range of 3309–3443 cm^{-1} and carbonyl peaks in the range of 1584–1638 cm^{-1}.

Capitellataquinone A (**1**) obtained as orange amorphous solid (m.p. 203–204 °C) analysed for $C_{20}H_{18}O_6$ by means of HREIMS. The aromatic region of the ^1H NMR spectrum, which was run in DMSO-d_6 (Table 1) showed the presence of four aromatic protons. Their multiplicity, an ABC system at δ 7.77 (1H, *dd*, *J* = 7.3, 8.2 Hz), δ 7.66 (1H, *d*, *J* = 7.3 Hz) and δ 7.34 (1H, *d*, *J* = 8.2 Hz), and a 1H singlet at δ 8.22, were suggestive of an anthraquinone with one monosubstituted and the other, a trisubstituted ring. A broad singlet at δ 12.81 indicated a *peri*-hydroxyl group to be one of the substituents. The presence of a chelated carbonyl, a non-chelated carbonyl, two oxygenated carbons and a hydroxymethyl group in the ^{13}C spectrum as well as DEPT-135 spectrum supported the earlier assignment of the protons. A ^3J bond correlation between H-5 (δ 7.66) and the non-chelated carbonyl C-10 (δ 183.5) as well as the absence of crosspeaks between H-1 and this carbon confirmed that the free hydroxyl group is located on C-8 and not C-5. For comparison with the spectra of capitellataquinone B–D, which were run in acetone-d_6, the ^1H NMR of capitellataquinone A was also run in this solvent. A ^3J correlation between H-1 (δ 8.22) and the hydroxymethyl carbon at δ 57.8 in the HMBC supported the assignment of the hydroxymethyl moiety at C-2, which is also biogenetically reasonable (Lu et al., 1998). Another ^3J correlation observed between H-1 and a deshielded quaternary carbon (δ 163.5) suggested the presence of an oxygenated substituent at C-3. An –OCH–CH_2– spin system was also evident from the ^1H and COSY spectrum. Correlations between the oxygenated methine and the methylene protons of this spin system to the quaternary carbons C-3 (δ 163.5) and C-4 (δ 130.1) supported the presence of a furan ring fused to the anthraquinone moiety. The presence of two isolated methyl groups (C-4′ and C-5′) belonging to a hydroxyisopropyl moiety of the furan ring located next to the methine proton was evident from the peaks at δ 1.15 and 1.17 and carbon signals at δ 25.6, 26.2 and 70.8 ppm. Other HMBC correlations within the furan ring as shown in Table 2 led to the assigned structure. Further confirmation of the structure was obtained from EIMS spectra where a fragment ion peak corresponding to the loss of C_3H_7O followed by a hydride transfer was observed at *m*/*z* 296 $[M - 59 + H]^+$ (Ito et al., 2000). Thus, capitellataquinone A was assigned as 2-hydroxymethyl-3,4-[2′-(1-hydroxy-1-methylethyl)-dihydrofurano]-8-hydroxyanthraquinone, a new furanoanthraquinone.



Cpd.	R_1	R_2	R_3
1	CH_2OH	H, H	OH
2	CH_2OH	H, OH	OH
3	CH_2OH	H, H	H
4	CH_3	H, H	H

Fig. 1. Capitellataquinone A–D (**1**–**4**).

Capitellataquinone B (**2**) was obtained as yellow amorphous solid (m.p. 165–166 °C) and analyzed for $C_{20}H_{18}O_7$ by means of HREIMS. The UV absorption spectrum resembles that of **1** suggesting a similar hydroxyl substitution pattern on the anthraquinone ring. The aromatic region of the ^1H NMR spectrum is similar to that of **1** revealing a monosubstituted ring A. Comparison of the proton and ^{13}C chemical shifts of **2** with those of **1** further revealed the presence of a hydroxymethyl group on C-2 and a hydroxyl group on C-8 as in **1**. ^3J correlations of H-1 (δ 8.50) to this hydroxymethyl

Table 1
^{1}H (Acetone-d_6, 500 MHz) and ^{13}C (acetone-d_6, 125 MHz) chemical shifts of capitellataquinone A–D (**1**–**4**)

δ_H (J, Hz)						δ_C				
H	1[d]	**1**	**2**	**3**	**4**	C	**1**[d]	**2**	**3**[c]	**4**[c]
1	8.22 *s*	8.40 *s*	8.50 *s*	8.31 *s*	8.02 *s*	1	126.9 (CH)[b]	127.9	127.5	130.6
2	–	–	–	–		2	130.4	132.0	[e]	125.8
3	–	–	–	–		3	163.5	162.7	163.5	164.2
4	–	–	–	–		4	130.1	131.1	[e]	[e]
5	7.66 *d* (7.3)	7.78 *dd* (7.5, 8.0)	7.81 *dd* (7.0, 3.0)	8.23 *ddd* (7.0, 7.0, 3.0)	8.27 *dd* (8.8, 2.5)	5	119.2 (CH)[b]	119.3	127.5	127.1
6	7.77 *dd* (7.3, 8.2)	7.78 *dd* (7.5, 8.0)	7.81 *dd* (7.0, 3.0)	7.87 *dd* (7.0, 3.0)	7.75*dd* (7.0, 3.0)	6	137.2 (CH)[b]	136.7	134.5	133.9
7	7.34 *d* (8.2)	7.33 *d* (8.0)	7.38 *dd* (7.0, 3.0)	7.87 *dd* (7.0, 3.0)	7.75 *dd* (7.0, 3.0)	7	124.4 (CH)[b]	124.6	134.5	133.9
8	–	–	–	8.23 *ddd* (7.0, 7.0, 3.0)	8.21 *dd* (8.8, 2.5)	8	161.0	161.0	127.5	127.1
9						9	187.9	188.1	181.5	182.2
10						10	183.5	184.7	[e]	[e]
11						11	134.1	134.1	[e]	133.5
12						12	116.4	116.1	[e]	133.5
13						13	126.1	126.9	[e]	[e]
14						14	128.9	130.3	130.1	129.0
1′	3.57 *d* (8.5)	3.73 *d* (8.5)	5.89 *d* (4.0)	3.71 *d* (8.5)	3.62 *dd* (18.2, 8.5) 3.75 *dd* (18.2, 8.5)	1′	31.7 (CH_2)[b]	71.9	71.8	32.3
2′	4.83 *t* (8.5)	4.98 *t* (8.5)	4.63 *d* (4.0)	4.92 *t* (8.5)	4.81 *t* (8.5)	2′	92.2 (CH)[b]	98.4	93.0	91.4
3′	–	–	–	–	–	3′	70.8	70.5	[e]	72.0
[a]4′	1.15 *s*	1..30	1.36 *s*	1.27 *s*	1.25*s*	[a]4′	25.6 (CH_3)[b]	24.8	25.0	24.0
[a]5′	1.17 *s*	1..32	1.37 *s*	1.32 *s*	1.38 *s*	[a]5′	26.2 (CH_3)[b]	25.3	26.0	26.0
CH_2OH	4.58 *br*	4.80 *br*	4.84 *br*	4.76 *d* (4.0)	–	CH_2OH	57.8 (CH_2)[b]	58.2	58.5	–
CH_3	–		–	–	2.35 *s*	CH_3	–	–	–	15.7
CH_2**OH**	5.50 *brs*	4.67 *brs*	4.68 *br*	4.45 *brs*	–					
3′-OH	4.68 *brs*	3.97 *brs*	4.00 *brs*	3.85 *brs*	3.87 *brs*					
8-OH	12.81 *brs*	12.96 *brs*	12.84 *brs*	–	–					

[a] The signals are interchangeable.
[b] Multiplicity from DEPT ^{13}C experiment.
[c] Indirect detection from HSQC and HMBC.
[d] Spectrum run in DMSO-d_6.
[e] NMR performed on cryoprobe; crosspeaks were not observable due to insufficient quantity of sample.

carbon (δ 58.2) and to the chelated carbonyl group (C-9; δ 188.1) supported this assignment. Another ^{3}J correlation of H-1 to an oxygenated carbon (δ 162.7) together with ^{1}H and ^{13}C signals as well COSY correlations supported a furanoanthraquinone skeleton with a hydroxyisopropyl moiety, as in **1**. Further support was derived from the EIMS spectrum from the peaks at *m/z* 312, $[M - 59 + H]^+$ in the EIMS spectrum indicating the loss of this moiety from C-1′ of the furan ring. In the aliphatic region of the ^{1}H NMR spectrum, the signal at δ 3.62 for the methylene proton of H-1′ in **1** was absent in **2**. Instead, an oxymethine-proton signal was indicated by the signal at δ 5.89. This was further supported by appearance of a carbon signal at δ 71.9 and the appearance of a doublet (J = 4.0 Hz) instead of a triplet for H-2′ (δ 4.63). H–H COSY crosspeaks between these two protons (δ 4.63 and 5.89) confirmed that they are vicinal methine protons. Based on its J value, a *trans* configuration was assigned to the molecule (Ito et al., 2000). Furthermore, the presence of crosspeaks between the methyl groups (δ 1.36 and 1.37) of the hydroxyisopropyl moiety with each of the methine proton (H-1′ and H-2′) in the NOESY experiment further supported a *trans* configuration. However, the absolute stereochemistry of the molecule was left undetermined. Other HMBC correlations as shown in Table 2 assigned capitellataquinone B as 2-hydroxymethyl-3,4-[1′-hydroxy-2′-(1-hydroxy-1-methylethyl)-dihydrofurano]-8-hydroxyanthraquinone.

Capitellataquinone C (**3**) was obtained as yellow oil after repetitive purification. It analysed for $C_{20}H_{18}O_5$ by means of HREIMS. The UV spectrum was similar to those of **1** and **2** except for the shift of absorbance maxima at 415 nm to 385 nm was no longer seen suggesting a different substitution pattern for the substituted hydroxyl group. The aromatic region of the ^{1}H NMR spectrum of **3** (Table 1) differs only slightly from

Table 2
HMBC and COSY (Acetone-d_6, 500 MHz) correlations of capitellataquinone A–D (**1–4**)

Compound H/C	**1**[b]			**2**			**3**			**4**		
	δ_H	HMBC	COSY	δ_H	HMBC	COSY	δ_H	[c]HMBC	COSY	δ_H	[c]HMBC	COSY
1	8.22	CH_2OH, C-14, C-3, C-9		8.50	CH_2OH, C-14, C-3, C-9		8.31	CH_2OH, C-14, C-3, C-9		8.02	CH_3, C-14, C-3, C-9	
5	7.66	C-12, C-7, C-10		7.81	C-7, C-10		8.23	C-7, C-6		8.27	C-7, C-6	
6	7.77	C-11, C-8		7.81	C-11, C-8		7.87	C-11, C-12		7.75	C-11, C-12	
7	7.34	C-12, C-5		7.38	C-12, C-5		7.87	C-11, C-12		7.75	C-11, C-12	
8	–			–			8.23	C-7, C-6		8.21	C-7, C-6	
1′	3.57	C-3′, C-2′, C-14, C-4	C-2′	5.89	C-3′	C-2′	3.71	C-3′, C-2′, C-14, C-3	C-2′	3.62	C-3′, C-2′, C-14, C-3	C-2′
2′	4.83	C-4, C-3	C-1′	4.63	C-1′, C-3	C-1′	4.92		C-1′	4.81		C-1′
[a]4′	1.15	C-3′, C-2′ C-5′		1.36	C-3′, C-2′, C-5′		1.27	C-3′, C-2′, C-5′		1.25	C-3′, C-2′, C-5′	
[a]5′	1.17	C-3′, C-2′ C-4′		1.37	C-3′, C-2′, C-4′		1.32	C-3′, C-2′, C-4′		1.38	C-3′, C-2′, C-4′	
CH_2OH	4.58	C-2		4.84	C-1, C-2, C-3	CH_2**OH**	4.76	–	CH_2**OH**			
2-CH_3	–			–			–			2.35	C-1, C-2, C-3	
CH_2**OH**	5.50	**CH_2**OH		4.68	CH_2OH, C-2	**CH_2**OH	4.45	–	**CH_2**OH			
3′-**OH**	4.68	C-4′/ C-5′ C-3′		4.00	C-4′/C-5′, C-3′		3.85			3.87		
8-OH	12.81			12.84	C-7, C-12, C-8		–			–		

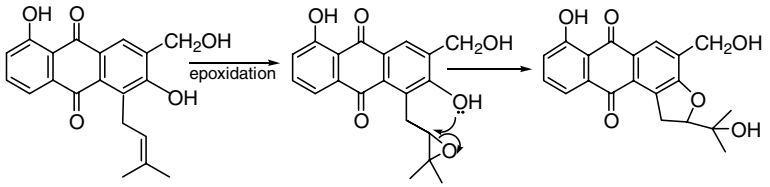
[a] The signals are interchangeable.
[b] Spectrum run in DMSO-d_6.
[c] HMBC carried out on cryoprobe; some crosspeaks are not observable.

those of **1** and **2** by the absence of the broad singlet at about δ 12.81 suggesting that the *peri*-hydroxyl group has been replaced by a proton and ring A is non-substituted, thus having an A_2B_2 system. Due to insufficient quantity of sample, ^{13}C signals were obtained indirectly from HSQC and HMBC correlations. In the HMBC experiment, the crosspeaks for some quaternary carbons were not observable. However, some important ^2J and ^3J HMBC correlations for H-1′, for the methyl protons and for H-8 as shown in Table 2 were observed. These correlations together with H–H COSY correlations and mass spectral data strongly supported the assignment of capitellataquinone C as 2-hydroxymethyl-3,4-[2′-1-hydroxy-1-methylethyl)-dihydrofurano] anthraquinone.

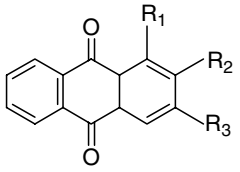
Capitellataquinone D (**4**), obtained as yellow oil, analysed for $C_{20}H_{18}O_4$ by means of HREIMS. The spot was bright yellow under long wavelength UV (366 nm). The UV absorption spectrum resembles that of **1–3** indicating an anthraquinone-type compound. The aromatic region of the ^1H NMR spectrum (Table 1) resembles that of **3** with a non-substituted ring A. The slight upfield shift of the isolated proton (δ 8.02) reflects a slightly shielded environment in ring C. The presence of two nonchelated carbonyls, one oxygenated carbon and the absence of a hydroxymethyl peak in addition to an upfield peak for methyl shift in the ^{13}C spectrum supported a furanoanthraquinone skeleton with an unsubstituted ring A and a methyl group at C-2 of ring C. The replacement of the hydroxymethyl group with a methyl group at C-2 justified the slight upfield shift of H-1 compared to compounds **1–3**. A ^3J correlation between H-1 (δ 8.02) and the methyl carbon (δ 15.7) and other correlations, as shown in Table 2 led to the assignment of capitellataquinone D as 2-methyl-3,4-[2′-(1-hydroxy-1-methylethyl)-dihydrofurano]anthraquinone.

The presence of a dihydrofuran ring in naphtoquinones, xanthones and flavonoids has been frequently reported (Ito et al., 2000; Peres et al., 2000; Abegaz et al., 2000). However, the presence of this moiety as part of an anthraquinone system is quite rare. As far as we know, there has only been one report on the occurrence of a natural furanoanthraquinone named Galiprenylin which was isolated from *Galium mollugo* (Rubiaceae). However, there was some ambiguity in the structure (Kuiper and Labadie, 1983). The biosynthesis of capitellataquinone A is rationalized in Scheme 1.

Four known anthraquinones, rubiadin (**5**), anthragallol 2-methyl ether (**6**), alizarin 1-methyl ether (**7**) and digiferruginol (**8**) as well as scopoletin were also isolated from the stems of *H. capitellata* (Schripsema et al., 1999; Ismail et al., 1997; El-Gamal et al., 1995).



Scheme 1. Proposed biosynthetic pathway for capitellataquinone A.



Cpd.	R_1	R_2	R_3
5	OH	CH_3	OH
6	OH	OCH_3	OH
7	OCH_3	OH	H
8	OH	CH_2OH	H
9	OH	CH_2OH	*O*-β-glucoside

Fig. 2. Compounds **5**–**9**.

From the roots of the plant, an anthraquinone glycoside, lucidin-3-*O*-β-glucoside (**9**) was isolated. Lu et al. (1998) has reported the isolation of this compound from *Rynchotechum vestitum* as the first from a natural source (see Fig. 2).

3. Experimental

3.1. General experimental procedures

Melting points were determined on a Kofler hot stage apparatus and were uncorrected. UV (in absolute EtOH) and IR spectra were recorded on Shimadzu UV–Vis 160 and Perkin–Elmer 1650 FTIR spectrometers, respectively. Optical rotation was measured on a JASCO DIP-370 digital polarimeter. Mass spectra were recorded on Jeol JMS DX 303 or Polaris Q Mass Spectrometers (ThermoFinnigan San Jose CA), with ionization being induced by electron impact at 70 eV. HREIMS were measured using Kratos MS80 or Varian MAT 312 double focusing spectrometers. ^{1}H NMR and ^{13}C NMR spectra (DMSO-d_6) were recorded on JEOL JNM A 500 or Varian Unity INOVA 500 Spectrometers at 500 (^{1}H) and 125 (^{13}C) MHz. For analytical and preparative TLC, Merck TLC plates Silica gel 60 F_{254} and Merck PLC plates Silica gel 60 F_{254} (2 mm) were utilized, respectively. For column chromatography (CC), Silica gel Merck 7734 or 9385 were used. The solvent systems used were either $CHCl_3$:MeOH gradient (solvent system I), hexane:EtOAc gradient followed by EtOAc:MeOH gradient (solvent system II), or DCM–MeOH gradient (solvent system III). For reverse phase CC, Merck 10167 was utilized using H_2O:MeOH (7:3) with gradient elution as the solvent system (solvent system IV).

3.2. Plant material

The stems and roots of *H. capitellata* were collected at the Forest Reserve of the Department of Wildlife, Rehabilitation Camp, Sungkai, Perak, Malaysia in May 2002. A voucher specimen (No. SK146/02) was prepared and deposited at the herbarium of Laboratory of Natural Products, Institute of Bioscience, Universiti Putra Malaysia, Serdang, Selangor, Malaysia.

3.3. Isolation

3.3.1. Compounds *1*–*8* and scopoletin

Fifteen kg of ground, air-dried stems were macerated in $CHCl_3$ for 48 h and the extraction was repeated three times. After removal of the solvent under reduced pressure, 90 g of crude chloroform extract was obtained, 80 g of which was directly subjected to CC (ID = 7 cm, silica gel, 1 kg), using solvent system I to give 56 fractions (Column 1). Fractions 20–27 (50 g), the major fractions from Column 1 were combined and further chromatographed on CC (ID = 7 cm, silica gel, 1 kg) using solvent system II to yield 163 fractions (Column 2). Fractions 135–147 (8 g) which eluted with 100% EtOAc were combined and rechromatographed on CC using solvent system III to yield Fractions A, B, C and D. Fraction C (2 g) was subjected to RP CC (ID = 2 cm, C-18 silica, 60 g) followed by repeated preparative TLC to yield 10 mg of **1**, 5 mg of **2**, 1 mg of **3** and 1 mg of **4**. CC of the less polar fractions of 15–20 (1.1 g) using the same solvent system followed by repeated preparative TLC yielded 8 mg of rubiadin (**5**). Fractions 40–48 (480 mg), 49–62 (690 mg) and 63–79 (1.27 g) from Column 2 were rechromatographed separately on CC using solvent system II. Further CC and repeated preparative TLC yielded a total of 5 mg of anthragallol 2-methyl ether (**6**), 20 mg of

alizarin 1-methyl ether (**7**) and 2 mg of digiferruginol (**8**). Fractions 128–134 (1.4 g) from Column 2 was subjected to repeated CC (ID = 2 cm, silica gel, 40 g) using solvent system II to yield 3 mg of scopoletin.

3.3.2. Compound 9

The dried roots (200 g) were macerated twice in MeOH and upon evaporation of solvent in vacuo yielded 6 g of dark-brown mass. The crude extract (3 g) was subjected to CC (ID = 3 cm, silica gel, 90 g) and eluted with solvent system II starting with hexane:EtOAc (7:3) to give 77 fractions. Fractions 40 and 41 were combined to yield a red-coloured mass partially soluble in methanol. The supernatant was transferred into another vial while the residue was recrystallized from acetone to yield 2 mg of lucidin-3-*O*-β-glucoside.

3.3.3. Capitellataquinone A (1)

10 mg, orange amorphous solid ($CHCl_3$); m.p. 203–204 °C; $[\alpha]_D^{25} = -277°$ (MeOH, *c* 1.3); HREIMS *m/z* reqd. 354.11034, obs. 354.11066; EIMS *m/z* (rel. int.): 354 (1), 337 (1), 321 (6), 312 (5), 296 (81), 278 (100); UV (EtOH) λ_{max} ($\log\varepsilon$): 248 (4.42), 280 (4.42), 415 (3.95) nm; UV (EtOH/NaOH) λ_{max}: 248, 280, 498 nm; IR ν_{max}^{KBr}, cm^{-1}: 3309 (OH), 2929 (C–H), 1584 (C=O), 1457, 1355, 1287, 1207, 1178, 1070, 1003, 870, 786; ^{13}C NMR (125 MHz, DMSO-d_6) and ^1H NMR (500 MHz, DMSO-d_6): Table 1; HMBC and COSY: Table 2.

3.3.4. Capitellataquinone B (2)

5 mg, yellow amorphous solid ($CHCl_3$); m.p. 165–166 °C; $[\alpha]_D^{25} = +77.7°$ (MeOH, *c* 1.8); HREIMS *m/z* reqd. 370.10525, obs. 370.09952; EIMS *m/z* (rel. int.): 370 (1), 337 (57), 312 (32), 294 (100), 265 (49); UV (EtOH) λ_{max}: 245 (3.19), 285 (3.55), 415 (3.06) nm; UV (EtOH/NaOH) λ_{max}: 216, 271 nm; IR ν_{max}^{KBr}, cm^{-1}: 3421 (OH), 2930 (C–H), 1603 (C=O), 1458, 1370, 1299, 1162, 1080, 1007, 975, 788; ^{13}C NMR (125 MHz, DMSO-d_6) and ^1H NMR (500 MHz, DMSO-d_6): Table 1; HMBC and COSY: Table 2.

3.3.5. Capitellataquinone C (3)

1 mg, yellow oil; $[\alpha]_D^{25} = -91.8°$ (MeOH, *c* 1.6); HREIMS *m/z* reqd. 338.11540, obs. 338.12057; EIMS *m/z* (rel. int.): 338 (1), 280 (100), 262 (88), 249 (82); UV (EtOH) λ_{max} ($\log\varepsilon$): 245 (3.96), 277 (3.97), 385 (3.17) nm; IR ν_{max}^{KBr}, cm^{-1}: 3440 (OH), 2933 (C–H), 1655 (C=O), 1291, 1207, 1066, 718, 607; ^{13}C NMR (125 MHz, DMSO-d_6) and ^1H NMR (500 MHz, DMSO-d_6): Table 1; HMBC and COSY: Table 2.

3.3.6. Capitellataquinone D (4)

1 mg, yellow oil; $[\alpha]_D^{25} = +128.6°$ (MeOH, *c* 1.4); HREIMS *m/z* reqd. 322.12050, obs. 322.11550; EIMS *m/z* (rel. int.) = 322 (13), 305 (42), 264 (100); UV (EtOH) λ_{max} ($\log\varepsilon$): 246 (3.94), 277 (4.0), 388 (3.16) nm; IR ν_{max}^{KBr}, cm^{-1}: 3433 (OH), 2930 (C–H), 2865 (C–H), 1638 (C=O), 1327, 1268, 1161, 1054, 1036, 878; ^{13}C NMR (125 MHz, DMSO-d_6) and ^1H NMR (500 MHz, DMSO-d_6): Table 1; HMBC and COSY: Table 2.

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