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Phytochemistry 68 (2007) 2426–2431

PHYTOCHEMISTRY

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Elucidation of excogallochaols A–D, four unusual diterpenoids from the Chinese mangrove *Excoecaria agallocha*

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Received 10 October 2006; received in revised form 2 March 2007
Available online 21 June 2007

Abstract

Diterpenoids, excoagallochaols A–D (**1**–**4**), with an unprecedented skeleton, were isolated from the ethyl acetate extract of the stems and leaves of the mangrove *Excoecaria agallocha* L. The structures of these metabolites were elucidated on the basis of detailed analysis of their spectroscopic data and by comparison with those of related compounds reported in literature.

Keywords: *Excoecaria agallocha*; *Euphorbiaceae*; Diterpenoid; Excoagallochaols A–D

1. Introduction

The mangrove shrub *Excoecaria agallocha* L. (*Euphorbiaceae*) is widely distributed on seashores and edges throughout tropical Africa, Asia, and northwest Australia. The bark and wood of *E. agallocha* have been used as a traditional medicine in treatment of flatulence in Thailand (Karalai et al., 1994; Wiriyachitra et al., 1985), while its leaves and latex have been used as a fish poison in India (Prakash et al., 1983). The piscicidal constituent, excoecariatoxin (Ohigashi et al., 1974) and some related daphnane diterpene esters known as skin irritants and tumor promoters, were isolated from the twigs, bark and latex of *E. agallocha* from Thailand (Karalai et al., 1994; Wiriyachitra et al., 1985) and Japan (Ohigashi et al., 1974; Konishi et al., 2000). Interestingly, a novel phorbol ester was also isolated as an anti-HIV principle from the leaves and stems of *E. agallocha*, collected in Northwest Australia (Erickson et al., 1995). More recently, a series of diterpenoid derivatives with different kinds of carbon skeleta such as the labdane, beyerane, isopimarane, and kaurane types, were isolated from the title plant (Anjaneyulu and Rao, 2000, 2003; Konishi et al., 1998, 2003; Konoshima et al., 2001).

In the course of our search for biologically active substances from Chinese marine organisms (Huang et al., 2004; Shao et al., 2002; Sun and Guo, 2004), a sample of the mangrove *E. agallocha* was collected from Guangxi Province of China. A chemical investigation of the EtOAc extract of the stems and leaves of the collected sample resulted in the isolation and structure elucidation of agallochaols A–J (Wang and Guo, 2004; Wang et al., 2005, 2006). Our continued investigation on this plant has now led to the isolation of four novel diterpenes, namely excoagallochaols A–D (**1**–**4**) (Fig. 1). In this paper, we report the isolation and structure elucidation of these compounds.

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doi:10.1016/j.phytochem.2007.05.015

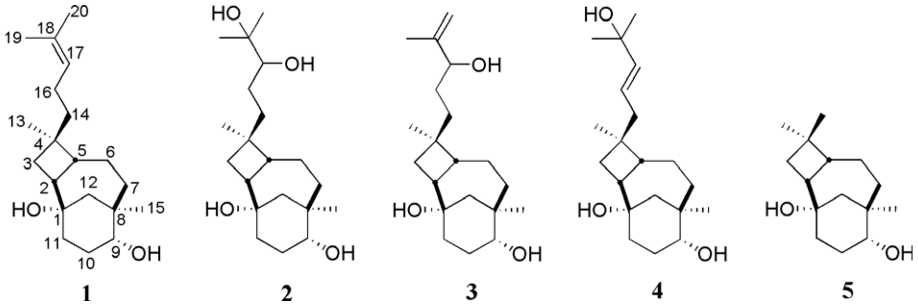

Fig. 1. Structures of excoagallochaols A–D (**1**–**4**) and sesquiterpenoid **5**.

2. Results and discussion

The powdered stems and leaves of *E. agallocha* were extracted exhaustively with MeOH. The MeOH extract was partitioned consecutively between H_2O and petroleum ether, H_2O and EtOAc, H_2O and *n*-BuOH, respectively. The ethyl acetate fraction was subjected to column chromatography over silica gel and Sephadex LH-20 to give the four pure compounds, named excoagallochaols A–D (**1**–**4**).

Excoagallochaol A (**1**) was isolated as a colorless oil. Its molecular formula $C_{20}H_{34}O_2$, deduced from the pseudo-molecular ions at m/z 329.2429 $[M+Na]^+$, which indicated four degrees of unsaturation. The IR absorption at 3442 cm^{-1} showed the presence of a hydroxyl group in the molecule. This was in agreement with the presence of a tertiary oxygenated carbon (δ 71.6, s) and a secondary oxygenated carbon (δ 73.3, d) as deduced from the ^{13}C NMR and DEPT spectra (Table 1). The ^{13}C NMR and DEPT spectra established the presence of a double bond (δ 125.5, d; 130.3, s), so the four degrees of unsaturation were due to one double bond and three rings in the molecule. In addition, 16 sp^3 carbons ($2 \times C$, $2 \times CH$, $8 \times CH_2$, and $4 \times CH_3$) resonating at higher field were fully assigned to their corresponding proton signals by HMQC experiments (Table 1).

Three fragments **a** (C-3/C-2/C-5/C-6/C-7), **b** (C-9/C-10/C-11), and **c** (C-14/C-16/C-17) were identified from the analysis of the 2D NMR spectra (HMQC, ^1H–^1H COSY and HMBC) (Fig. 2). For partial structure **a**, connectivity from H_2-3 to H_2-7 was evident from the DQF-COSY spectrum. The proton connectivities of **b** and **c** were deduced from the clear cross peaks of H_2-10 (δ 1.96, m) to H-9 (δ 3.59, br s) and H_2-11 (δ 2.63, ddd, $J = 14.2$, 10.8, 3.6; 1.73, m), as well as H_2-16 (δ 2.03, m) to H_2-14 (δ 1.63, m) and H-17 (δ 5.24, br t, $J = 6.8$), in the DQF-COSY spectrum of **1** (Fig. 2). The HMBC correlations were applied to confirm the assignments for the structural fragments **a**–**c** in those cases where the overlapping proton signals were not sufficient to prove these structural fragments by HMQC and ^1H–^1H COSY spectroscopic analysis alone. Finally, the linkage of the fragments **a**–**c**, the isopropenyl, as well as the "loose ends", resulting from the insertion of the tertiary and quaternary carbons of C-1, C-4, and C-8 into the fragments, could be fully connected by HMBC experiments.

The HMBC correlations of H-2 with C-1, C-11, H_2-11 with C-1, C-2, and H_3-15 with C-7, C-8, and C-9, indicated the connection of the partial structures **a** and **b** with the oxygenated tertiary carbon C-1 as well as the quaternary

Table 1
^1H and ^{13}C NMR data[a] for excoagallochaol A (**1**)

No.	In C_5D_5N[b]			In $CDCl_3$[c]		
	δ^1H (mult., J (Hz))	$\delta^{13}C$	DEPT[d]	δH (mult., J (Hz))	$\delta^{13}C$	DEPT[d]
1		71.6	C		72.5	C
2	2.70 m	42.7	CH	2.43 m	41.8	CH
3α	2.07 m	34.1	CH_2	1.70 m	33.2	CH_2
3β	2.10 m			1.70 m		
4		36.7	C		37.1	C
5	1.97 m	47.5	CH	1.82 m	47.3	CH
6α	1.41 m	22.4	CH_2	1.42 m	22.2	CH_2
6β	1.97 m			1.82 m		
7α	1.56 m	36.4	CH_2	1.50 m	36.1	CH_2
7β	1.17 m			1.05 m		
8		37.7	C		37.6	C
9	3.59 br s	73.3	CH	3.32 br s	74.0	CH
10α	1.96 m	27.9	CH_2	1.81 m	27.1	CH_2
10β	1.96 m			1.67 m		
11α	2.63 ddd (14.2, 10.8, 3.6)	37.1	CH_2	1.82 m	35.8	CH_2
11β	1.73 m			1.43 m		
12α	2.03 ov[e]	38.7	CH_2	1.25 d (13.7)	38.4	CH_2
12β	2.17 d (13.6)			1.82 m		
13	0.98 s	21.1	CH_3	0.91 s	21.4	CH_3
14a	1.63 m	41.2	CH_2	1.50 m	41.1	CH_2
14b	1.63 m			1.50 m		
15	1.26 s	30.9	CH_3	0.99 s	30.1	CH_3
16a	2.03 m	23.8	CH_2	1.86 m	23.8	CH_2
16b	2.03 m			1.86 m		
17	5.24 br t (6.8)	125.5	CH	5.12 m	124.8	CH
18		130.3	C		130.9	C
19	1.60 s	17.3	CH_3	1.60 s	17.8	CH_3
20	1.69 s	25.4	CH_3	1.68 s	25.8	CH_3

[a] *Bruker-DRX-400* NMR spectrometer; assignments made by HMQC and HMBC experiments.

[b] Chemical shifts referred to residual C_5H_5N (δ 7.19, 7.56, 8.70 ppm) and C_5D_5N (δ 123.1, 135.1, 149.5 ppm), respectively.

[c] Chemical shifts referred to residual $CHCl_3$ (δ 7.26 ppm) and $CDCl_3$ (δ77.0 ppm), respectively.

[d] By DEPT sequence.

[e] Overlapped signals.

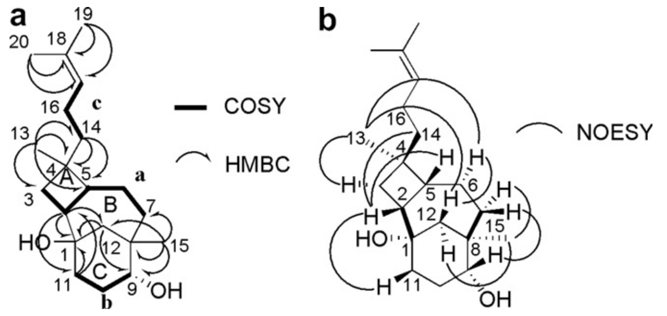

Fig. 2. The ^1H–^1H COSY and selected HMBC (a), and key NOESY (b) correlations of **1**.

carbon C-8. The distinct long range correlations of H_2-12 with C-1, C-8, and both H-2 and H_3-15 with C-12 suggested a carbon bridge of C-1/C-12/C-8, which resulted in the formation of rings B and C in the structure. Partial fragment **c** was linked to the isopropenyl group based on the long range correlations of both H_3-19 and H_3-20 with C-17 and C-18, to form the side-chain of the structure. Finally, the clear HMBC correlation of H_3-13/C-3, C-4, C-5 and C-14, and H_2-14/C-4 and C-5, led to the connection from the side-chain to both C-3 and C-5 of fragment **a** through the quaternary carbon C-4, which consequently established ring A and the planar skeleton of **1**.

The relative stereochemistry of **1** was subsequently elucidated by NOESY experiments (Fig. 2). The NOE cross peaks for the H_3-13 to H-3α and H-6α indicated the α-configuration of these protons. An α-oriented C-15 methyl group was deduced from the NOE correlation between H_3-15 and H-12α, and non-NOE between H_3-15 and H-9β. Furthermore, the NOE correlations for H-12β to H-6α and H_3-13 suggested a β-bridge for ring B, and consequently, established the α-configuration for OH-1. Finally, the NOE cross peak of H-2/H-11β and H_2-14, and H-7β/H-9, indicated the β-configuration for these protons, as well as a *cis*-fusion for rings A and B.

The assignments of the ^1H and ^{13}C NMR spectroscopic data and the relative stereochemistry of **1** were further confirmed by comparison with those of the related sesquiterpenoid **5**, isolated previously from the ethereal extract of other species as *Panax ginseng* (Iwabuchi et al., 1990) or *Senecio crassissimus* (Bohlmann and Ziesche, 1981). The relevant NMR data of the core skeleton of **1** were identical with those of **5**, with the additional signals being assigned to the side-chain, namely the subfragment of an isoamylene. All of these data confirm structure **1** (Table 1, and Fig. 2) for excoagallochaol A.

A modified Mosher's method was attempted to determine the absolute configuration of the secondary hydroxy group at C-9. Unfortunately, the experiment was unsuccessful due to the limited amount of the sample.

Excoagallochaol B (**2**) was shown to be the 17,18-dihydroxy form of excoagallochaol A. The HRESIMS of **2** established the molecular formula $C_{20}H_{36}O_4$ by the presence of the pseudo-molecular ion $[M+Na]^+$ at *m*/*z* 363.2515, indicating one degree of unsaturation less and 34 mass units more than that of **1**. Analysis of the ^1H and ^{13}C NMR spectroscopic data of **2** (Table 2) established a great similarity to those of **1**, deviating only in the side-chain, where the trisubstituted double bond in **1** (δ_H 5.24, br t, $J = 6.8$ Hz; δ_C 130.3, s, and 125.5, t) was replaced by a CH–O (δ_H 3.75 br d, $J = 8.9$; δ_C 79.5, d) and a C–O group (δ 72.5, s) in **2**. The hydroxylation at Δ^{17} caused the two vinyl methyls resonating at δ 1.60 (s) and 1.69 (s) in **1** remarkably upfield shifted to δ 1.50 (s) and 1.53 (s) in **2**, respectively. This evidence suggested that compound **2** was derived from **1** with its Δ^{17} double bond being dihydroxylated. This conclusion was supported by the proton connectivity of H_2-14/H_2-16/H-17 in the ^1H–^1H COSY spectrum, as well as the long range correlations of both H_3-19 and H_3-20 with C-17 and C-18 in the HMBC spectrum, thus establishing the structure of excoagallochaol B.

Excoagallochaol C (**3**) was shown to be an 18(20)-dehydration derivative of excoagallochaol B (**2**). Its molecular

Table 2
^1H and ^{13}C NMR data[a] for excoagallochaol B (**2**)

No.	In C_5D_5N[b]			In CD_3OD[c]		
	δ^1H (mult., *J* (Hz))	$\delta^{13}C$	DEPT[d]	δH (mult., *J* (Hz))	$\delta^{13}C$	DEPT[d]
1		71.6	C		73.7	C
2	2.77 m	42.7	CH	2.44 m	43.3	CH
3α	2.13 m	34.5	CH_2	1.69 m	35.1	CH_2
3β	2.13 m			1.76 m		
4		36.7	C		37.9	C
5	2.02 m	47.3	CH	1.88 m	48.5	CH
6α	1.37 m	22.4	CH_2	1.40 m	23.5	CH_2
6β	1.98 m			1.88 m		
7α	1.54 m	36.4	CH_2	1.50 m	37.8	CH_2
7β	1.10 m			1.05 m		
8		37.7	C		38.7	C
9	3.56 br s	73.3	CH	3.24 br s	75.0	CH
10α	1.88 m	27.8	CH_2	1.84 m	28.0	CH_2
10β	1.86 m			1.61 m		
11α	2.58 m	37.0	CH_2	1.84 m	37.2	CH_2
11β	1.61 m			1.36 m		
12α	2.02 m	38.7	CH_2	1.32 m	38.7	CH_2
12β	2.17 m			1.84 m		
13	1.03 s	21.4	CH_3	0.91 s	22.1	CH_3
14a	2.40 m	38.9	CH_2	1.93 m	39.7	CH_2
14b	1.76 m			1.44 m		
15	1.25 s	31.7	CH_3	0.96 s	31.1	CH_3
16a	1.98 m	27.5	CH_2	1.59 m	28.1	CH_2
16b	1.73 m			1.20 m		
17	3.75 br d (8.9)	79.5	CH	3.21 dd (10.4, 1.3)	80.7	CH
18		72.5	C		74.2	C
19	1.50 s	25.7	CH_3	1.12 s	25.4	CH_3
20	1.53 s	25.7	CH_3	1.16 s	25.8	CH_3

[a] *Bruker-DRX-400* NMR spectrometer; assignments made by HMQC and HMBC experiments.

[b] Chemical shifts referred to residual C_5H_5N (δ 7.19, 7.56, 8.70 ppm) and C_5D_5N (δ 123.1, 135.1, 149.5 ppm), respectively.

[c] Chemical shifts referred to residual CH_3OH (δ 3.30 ppm) and CD_3OD (δ 49.0 ppm), respectively.

[d] By DEPT sequence.

formula $C_{20}H_{34}O_3$ was deduced from the pseudo-molecular ion $[M+Na]^+$ at *m*/*z* 345.2377 in the HRESIMS spectrum, in agreement with the molecular weight difference of 18 mass units observed between them. Four degrees of unsaturation were attributed to one terminal double bond (δ_H 4.97, 4.87, each s; δ_C 147.6, s, and 111.2, t) and three rings in the molecule. Both the ^1H and ^{13}C NMR spectra of **3** (Table 3) were closely related to those of **2**, suggesting the same polycyclic skeleton. A comparison of overall ^1H and ^{13}C NMR spectroscopic data (Tables 2 and 3) established that differences between **3** and **2** resided only at the side-chain. The appearance of two sp^2 carbon atoms (δ_C 147.6, s; 111.2, t) in the ^{13}C NMR of **3** and the disappearance of the tertiary oxygenated carbon (δ 74.2, s) in that of **2** clearly indicated the loss of one molecule of water at C-18/C-20. This conclusion was strongly supported by the remarkable downfield shift of H_3-19 (δ 1.75, s), and further confirmed by the HMBC correlations of H_3-19/C-17, C-18, C-20, and H_2-20/C-17, C-18, C-19.

Excoagallochaol D (**4**) was an isomer of excoagallochaol C (**3**). Its molecular formula $C_{20}H_{34}O_3$, deduced from the pseudo-molecular ion $[M+Na]^+$ at *m*/*z* 345.2377 in the HRESIMS spectrum, was the same as that of **3**. A comparison of the ^1H and ^{13}C NMR spectra of **4** (Table 3) with those of **2** indicated that the differences between them, like **3** and **2,** also involved the side-chain. The appearance of a pair of signals corresponding to a *trans* double bond (δ_H 5.69, d, $J = 15.7$ Hz; 5.64, dt, $J = 15.7$, 6.4 Hz; δ_C 124.0, d; 140.5, d) in **4** and disappearance of a secondary oxygenated carbon (δ_H 3.75 br d, $J = 8.9$; δ_C 79.5, d) in **2** led to location of the double bond at $\Delta^{16(17)}$. The obvious proton sequence of H_2-14/H-16/H-17 observed in the ^1H–^1H COSY spectrum of **4** supported the above conclusion. The structure of **4** was thus determined as an isomer of **3** with the loss of a molecule of water at C-16/C-17 of **2**.

Table 3
^1H and ^{13}C NMR data[a,b] for excoagallochaols C (**3**) and D (**4**)

No.	Excoagallochaol C (**3**)			Excoagallochaol D (**4**)		
	δ^1H (mult., *J* (Hz))	$\delta^{13}C$	DEPT[c]	δH (mult., *J* (Hz))	$\delta^{13}C$	DEPT[c]
1		72.5	C		72.4	C
2	2.46 m	41.6	CH	2.47 m	41.4	CH
3α	1.72 m	33.1	CH_2	1.75 m	32.6	CH_2
3β	1.72 m			1.75 m		
4		36.7	C		37.1	C
5	1.83 m	47.1	CH	1.87 m	46.9	CH
6α	1.83 m	22.0	CH_2	1.85 m	21.9	CH_2
6β	1.43 m			1.45 m		
7α	1.56 m	36.0	CH_2	1.54 m	36.0	CH_2
7β	1.03 m			1.04 m		
8		37.5	C		37.5	C
9	3.35 br s	73.9	CH	3.36 br s	73.9	CH
10α	1.83 m	27.0	CH_2	1.85 m	27.0	CH_2
10β	1.70 m			1.72 m		
11α	1.85 m	35.8	CH_2	1.87 m	35.7	CH_2
11β	1.45 m			1.47 m		
12α	1.37 m	38.3	CH_2	1.37 d (13.7)	38.4	CH_2
12β	1.83 m			1.87 m		
13	0.92 s	21.3	CH_3	0.92 s	21.6	CH_3
14a	1.65 m	36.6	CH_2	2.25 d (6.4)	43.2	CH_2
14b	1.65 m			2.25 d (6.4)		
15	1.02 s	30.0	CH_3	1.03 s	30.0	CH_3
16a	1.53 m	30.4	CH_2	5.64 dt (15.7, 6.4)	124.0	CH
16b	1.48 m					
17	4.06 br t (6.0)	76.6	CH	5.69 d (15.7)	140.5	CH
18		147.6	C		70.8	C
19	1.75 s	17.5	CH_3	1.34 s	30.0	CH_3
20a	4.97 s	111.2	CH_2	1.34 s	30.0	CH_3
20b	4.87 s					

[a] *Bruker-DRX-400* NMR spectrometer; chemical shifts referred to residual $CHCl_3$ (δ 7.26 ppm) and $CDCl_3$ (δ 77.0 ppm), respectively.

[b] Assignments made by HMQC and HMBC experiments.

[c] By DEPT sequence.

As mentioned above, *E. agallocha* proved to be a rich source of diterpenoids. A series of diterpenoids with different carbon skeletons, such as daphnane, labdane, beyerane, isopimarane/*ent*-isopimarane, atisane/*ent*-atisane, and kaurane, have been isolated from the title plant. Our previous investigation of the same sample also led to the isolation of some dozens of diterpenes belonging to the structural classes of isopimarane/*ent*-isopimarane, atisane/*ent*-atisane, as well as *ent*-secoatisane (Wang and Guo, 2004; Wang et al., 2005, 2006). The close biogenetic relationship between the above-mentioned metabolites is obvious. Interestingly, the newly discovered excoagallochaols A–D (**1**–**4**) display an unprecedented framework that is formally quite different from those described before, indicating that the biosynthetic pathway of excoagallochaols A–D is probably different from that of diterpenoids previously found in the species.

The discovery of excoagallochaol A–D (**1**–**4**) is an important addition to a diverse and complex array in the rapidly expanding class of known diterpenoids. Further studies should be conducted to prove the biosynthetic origin of these compounds and to understand their real ecological roles played in the life cycle of the plant, as well as to confirm their unusual structures by total synthesis.

3. Experimental

3.1. General experimental procedures

IR spectra were recorded on a Nicolet Magna FT-IR 750 spectrometer (ν_{max} in cm^{-1}); The NMR spectra were recorded on a Bruker-DRX-400 spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C. Chemical shifts are reported in parts per million (δ), using the residual $CHCl_3$ (δ_H 7.26 ppm), CH_3OH (δ_H 3.30 ppm) or C_5H_5N (δ_H 7.19, 7.56, 8.70 ppm) as an internal standard for ^1H NMR, and $CDCl_3$ (δ_C 77.0 ppm), CD_3OD (δ_C 49.0 ppm) or C_5D_5N (δ_C 123.1, 135.1, 149.5 ppm) for ^{13}C NMR; coupling constant (J) in Hz. ^1H and ^{13}C NMR assignments were supported by ^1H–^1H COSY, HMQC, HMBC, and NOESY experiments. The ESIMS and HRESIMS spectra were taken on a Q-TOF Micro LC–MS–MS mass spectrometer. Optical rotation was measured on a Perkin–Elmer 341 polarimeter. Commercial silica gel (Qing Dao Hai Yang Chemical Group Co., 100–200 and 200–300 mesh) was used for column chromatography. Precoated silica gel plates (Yan Tai Zi Fu Chemical Group Co., G60 F-254) were used for analytical TLC.

3.2. Plant material

Plant material was collected in the Guangxi Province, China, in 1999, and identified as *E. agallocha* L. by Prof. Jin-Gui Shen of Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences. A voucher specimen (GX-17) is available for inspection at the Institute of Materia Medica, SIBS-CAS.

3.3. Extraction and isolation

Dried ground stems and leaves (4.0 kg) of *E. agallocha* were extracted with MeOH (5 L × 3). The MeOH extract was concentrated *in vacuo* to give a residue (410 g) which was dissolved in H_2O (1000 ml) and the solution was partitioned consecutively between H_2O and petroleum ether, H_2O and EtOAc, H_2O and *n*-BuOH. The EtOAc extract was evaporated *in vacuo* to give a residue (100 g), which was separated by column chromatography (CC) on silica gel (100–200 mesh, 1.5 kg). The column was eluted with a gradient of petroleum ether–EtOAc (9:1–1:1) and Me_2CO to give 16 fractions on the basis of TLC checking. Fraction 8 was further purified by Sephadex LH-20 (MeOH), followed by silica gel CC ($CHCl_3$–MeOH, 98:2–95:5) to give **1** (2.5 mg). Compound **2** (6.0 mg) was obtained from fraction 13 after repeated Sephadex LH-20 CC (MeOH) and silica gel CC eluted with $CHCl_3$–MeOH (95:5–85:15). Fraction 9 was firstly subjected to Sephadex LH-20 (MeOH), and then splitting into **3** (3.5 mg) and **4** (3.0 mg), by silica gel CC ($CHCl_3$–MeOH, 98:2–90:10).

3.3.1. Excoagallochaol A (1)

Colorless oil; $[\alpha]_D^{20}$ −13 (MeOH; *c* 0.36); IR ν_{max} (KBr): 3442, 2920, 2850 cm^{-1}; For ^1H and ^{13}C NMR (C_5D_5N and $CDCl_3$, 400 and 100 MHz) spectra, see Table 1; ESIMS: *m/z* (rel. int.) 329.3 $[M+Na]^+$ (60); HRESIMS: *m/z* 329.2429 $[M+Na]^+$ (calcd for $C_{20}H_{34}O_2Na$, 329.2457).

3.3.2. Excoagallochaol B (2)

Colorless oil; $[\alpha]_D^{20}$ −4 (MeOH; *c* 0.16); IR ν_{max} (KBr): 3393, 2926, 2868 cm^{-1}. For ^1H and ^{13}C NMR (C_5D_5N and CD_3OD, 400 and 100 MHz) spectra, see Table 2; ESIMS: *m/z* (rel. int.) 363.3 $[M+Na]^+$ (50); HRESIMS: *m/z* 363.2515 $[M+Na]^+$ (calcd for $C_{20}H_{36}O_4Na$, 363.2511).

3.3.3. Excoagallochaol C (3)

Colorless oil; $[\alpha]_D^{20}$ +20 ($CHCl_3$; *c* 0.15); IR ν_{max} (KBr): 3384, 2925, 2868 cm^{-1}. For ^1H and ^{13}C NMR ($CDCl_3$, 400 and 100 MHz) spectra, see Table 3; ESIMS: *m/z* (rel. int.) 345.2 $[M+Na]^+$ (80); HRESIMS: *m/z* 345.2377 $[M+Na]^+$ (calcd for $C_{20}H_{34}O_3Na$, 345.2406).

3.3.4. Excoagallochaol D (4)

Colorless oil; $[\alpha]_D^{20}$ +2 ($CHCl_3$; *c* 0.15); IR ν_{max} (KBr): 3387, 2926, 2867 cm^{-1}. For ^1H and ^{13}C NMR ($CDCl_3$, 400 and 100 MHz) spectra, see Table 3; ESIMS: *m/z* (rel. int.) 345.3 $[M+Na]^+$ (90); HRESIMS: *m/z* 345.2377 $[M+Na]^+$ (calcd for $C_{20}H_{34}O_3Na$, 345.2406).

Acknowledgements

This research work was financially supported by the *National Marine "863" Project* (Nos. 2006AA09Z447 and 2006AA09Z412), *STCSM Project* (No. 054307062), and partly founded by the *State Key Program of Basic Research of China* (No. 2004CB518905).

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