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FOUR NEW COMPOUNDS FROM *POUZOLZIA ZEYLANICA* (L.) BENN. VAR. *MICROPHYLLA*

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Abstract – Two new stilbenes, pouzolignan D (**1**) and K (**2**), and two new norlignans, pouzolignan L (**3**) and M (**4**), together with four known flavonoids, rhamnocitrin (**5**), rhamnetin (**6**), isorhamnetin (**7**) and quercetin(**8**), were isolated from the aerial parts of *Pouzolzia zeylanica* (L.) Benn. var. *microphylla* (Wedd.) W. T. Wang. Their structures were elucidated by spectroscopic methods, including UV, IR, HR-ESI-TOF-MS, 1D and 2D NMR experiments.

INTRODUCTION

Pouzolzia zeylanica (L.) Benn. var. *microphylla* (Wedd.) W. T. Wang (Urticaceae), one of the four medicinal plants in the genus *Pouzolzia*, is extensively distributed in Japan, India, Malaysia, Indonesia, Australia and South China.[1, 2] It has been traditionally used for the treatment of gangrenous ulcers, sores, boils, diarrhea, syphilis, gonorrhea, etc.[3-5] A series of compounds including flavonoids, lignans, norlignans and triterpenoids have been isolated from this species and the genus Pouzolzia.[6-11] Previously, we reported the pharmacological activities of the extracts from *Pouzolzia zeylanica* var. *microphylla*, investigating its anti-inflammatory and analgesic effects,[12] therapeutic effects on mouse subcutaneous abscess[13] and skin ulcers in rats.[14] As part of our continuing study of this plant, two new stilbenes, pouzolignan D (**1**) and K (**2**), and two new norlignans, pouzolignan L (**3**) and M (**4**), along with four known flavonoids (**5-8**) (Figure 1) were obtained. Herein, we reported the isolation, structure elucidation of the four new compounds.

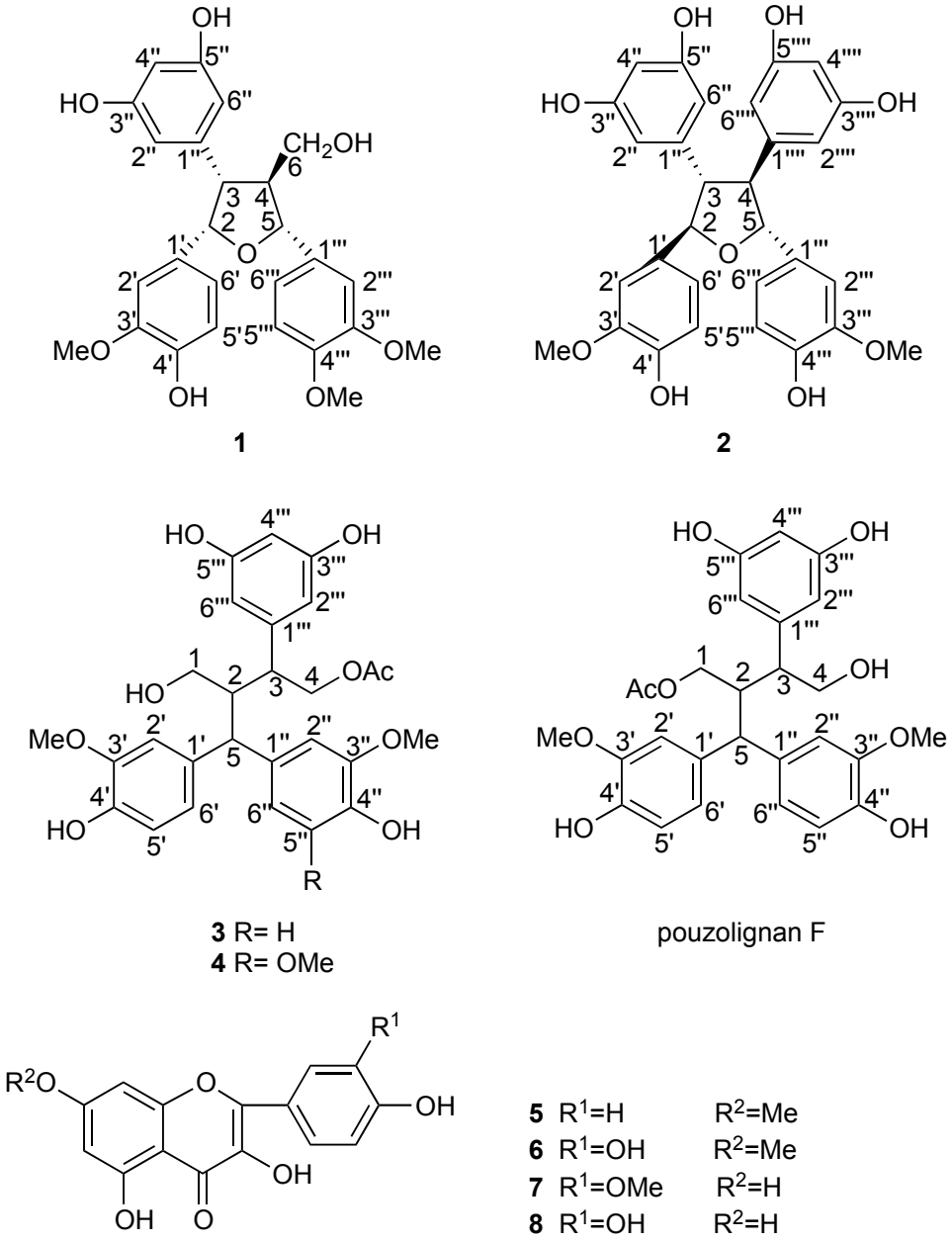

Figure 1. The structures of compounds **1-8**

RESULTS AND DISCUSSION

The aerial parts of *P. zeylanica* var. *microphylla* were extracted with petroleum ether and EtOAc, respectively. The resulting EtOAc extract was chromatographed on silica gel, RP-C_{18}, sephadex LH-20 and preparative RP-C_{18} HPLC to yield compounds **1-8**.

Compound **1** was obtained as brown amorphous powder. Its molecular formula was established as $C_{26}H_{28}O_8$ by HR-ESI-TOF-MS ([M-H]$^-$, *m/z* 467.1729) and had 13 degrees of unsaturation. The IR spectrum showed the presence of hydroxy group (3360 cm^{-1}), aromatic ring (1608, 1520 and 1455 cm^{-1}).

The ^{1}H NMR spectrum (Table 1) showed two 1,3,4-trisubstituted phenyl rings signals (ABX system) at δ_H 7.31 (1H, d, J = 2.0 Hz, H-2‴), 7.19 (1H, dd, J = 8.5, 2.0 Hz, H-6‴), 6.98 (1H, d, J = 8.5 Hz, H-5‴) and 6.78 (1H, d, J = 1.5 Hz, H-2′), 6.72 (1H,dd, J = 8.0, 1.5 Hz, H-6′), 6.61 (1H, d, J = 8.0 Hz, H-5′), one 1,3,5-trisubstituted phenyl ring signal (AB_2 system) at δ_H 6.10 (2H, d, J = 2.0 Hz, H-2″, 6″), 6.01 (1H, t, J = 2.0 Hz, H-4″) and three methoxy groups signals at δ_H 3.87, 3.83, 3.68 (each 3H, s). Since three phenyl rings accounted for 12 out of 13 degrees of unsaturation, the molecule was tetracyclic. NMR and HSQC spectra showed the presence of four methines signals at δ_H 2.52 (1H, m, H-4) with δ_C 57.0 (C-4), δ_H 3.62 (1H, m, H-3) with δ_C 53.7 (C-3), δ_H 4.90 (1H, d, J = 8.5 Hz, H-5) with δ_C 81.8 (C-5), δ_H 5.20 (1H, d, J = 7.5 Hz, H-2) with δ_C 83.4 (C-2), which indicated the existence of a tetrahydrofuran ring, and another methylene signal at δ_H 3.80 (2H, m, H-6) with δ_C 61.3 (C-6) were recognized.

The NMR data suggested that compound **1** had the same fundamental skeleton as the known compound cestrumoside.[15] The difference between them was **1** had three phenyl rings but cestrumoside had two, and their substituents on the phenyl rings were different. Comparison of the NMR data of **1** with those of cestrumoside showed that C-3 (δ_C 53.7) was shifted downfield 20.3 ppm, which suggested another phenyl ring attached on C-3 of the tetrahydrofuran ring. And it was confirmed by the HMBC correlations between H-3 and C-1″and C-2″, 6″. The position of the hydroxy and methoxy groups in compound **1** were established by extensive analysis of the HMBC spectra (Figure 2). The relative *trans* configuration between the methine protons at C-3 and C-4, C-4 and C-5, and *cis* configurantion between the methine protons at C-2 and C-3, C-2 and C-5 were established by the 2D NOESY spectral analysis. Thus, the structure of **1**, named pouzolignan D, was elucidated as 5-(3,4-dimethoxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-3-(3,5-dihydroxyphenyl)-4-(hydroxymethyl)tetrahydrofuran.

Compound **2** was obtained as a brown tabular crystal ($CHCl_3$-MeOH 1:1) and had a molecular formula of $C_{30}H_{28}O_9$ established by HR-ESI-TOF-MS ($[M+Na]^+$, *m/z* 555.1608, $[M-H]^-$, *m/z* 531.1740), correspongding to 17 degrees of unsaturation. The IR spectrum showed the presence of hydroxy group (3351 cm^{-1}), aromatic ring (1605, 1516 and 1459 cm^{-1}). In the ^{1}H NMR spectrum (Table 1), two sets of aromatic rings signals at δ_H 6.85 (2H, d, J = 1.5 Hz, H-2′, 2‴), 6.80 (2H, dd, J = 8.5, 1.5 Hz, H-6′, 6‴), 6.76 (2H, d, J = 8.5 Hz, H-5′, 5‴) and 6.11 (4H, d, J = 2.0 Hz, H-2″, 6″, 2⁗, 6⁗), 6.09 (2H, t, J = 2.0 Hz, H-4″, 4⁗) were recognized, revealing a 1,3,4-trisubstituted phenyl ring (ABX system) and a 1,3,5-trisubstituted phenyl ring (AB_2 system), respectively, as well as one methoxy group signal at δ_H 3.80 (6H, s, 3′, 3‴-OMe). Moreover, the ^{13}C NMR and DEPT spectra showed ten olefinic carbon signals at

Table 1. NMR spectral data for compounds **1, 2**

(δ in ppm, J in Hz. 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR)

position	**1**[a]		position	**2**[b]	
	δ_C	δ_H		δ_C	δ_H
2	83.4	5.20 (1H, d, 7.5)	2(5)	88.6	5.22 (2H, dd, 6.5, 3.0)
3	53.7	3.62 (1H, m)	3(4)	63.3	3.44 (2H, dd, 6.5, 3.0)
4	57.0	2.52 (1H, m)			
5	81.8	4.90 (1H, d, 8.5)			
6	61.3	3.80 (2H, m)			
1′	131.4		1′ (1‴)	133.9	
2′	110.7	6.78 (1H, d, 1.5)	2′ (2‴)	110.4	6.85 (2H, d, 1.5)
3′	146.5		3′ (3‴)	146.6	
4′	145.0		4′ (4‴)	148.3	
5′	113.8	6.61 (1H, d, 8.0)	5′ (5‴)	115.5	6.76 (2H, d, 8.5)
6′	119.3	6.72 (1H, dd, 8.0, 1.5)	6′ (6‴)	119.4	6.80 (2H, dd, 8.5, 1.5)
1″	144.3		1″ (1⁗)	141.1	
2″ (6″)	108.1	6.10 (2H, d, 2.0)	2″ (6″,2⁗,6⁗)	107.3	6.11 (4H, d, 2.0)
3″ (5″)	157.7		3″ (5″,3⁗,5⁗)	158.9	
4″	100.2	6.01 (1H, t, 2.0)	4″ (4⁗)	101.8	6.09 (2H, t, 2.0)
1‴	134.5				
2‴	110.6	7.31 (1H, d, 2.0)			
3‴	149.3				
4‴	148.7				
5‴	111.7	6.98 (1H, d, 8.5)			
6‴	118.7	7.19 (1H, dd, 8.5, 2.0)			
3′-OMe	55.1	3.68 (3H, s)	3′ (3‴)-OMe	55.8	3.80 (6H, s)
3‴-OMe	55.4	3.87 (3H, s)			
4‴-OMe	55.2	3.83 (3H, s)			

[a] in CD_3COCD_3, [b] in CD_3OD.

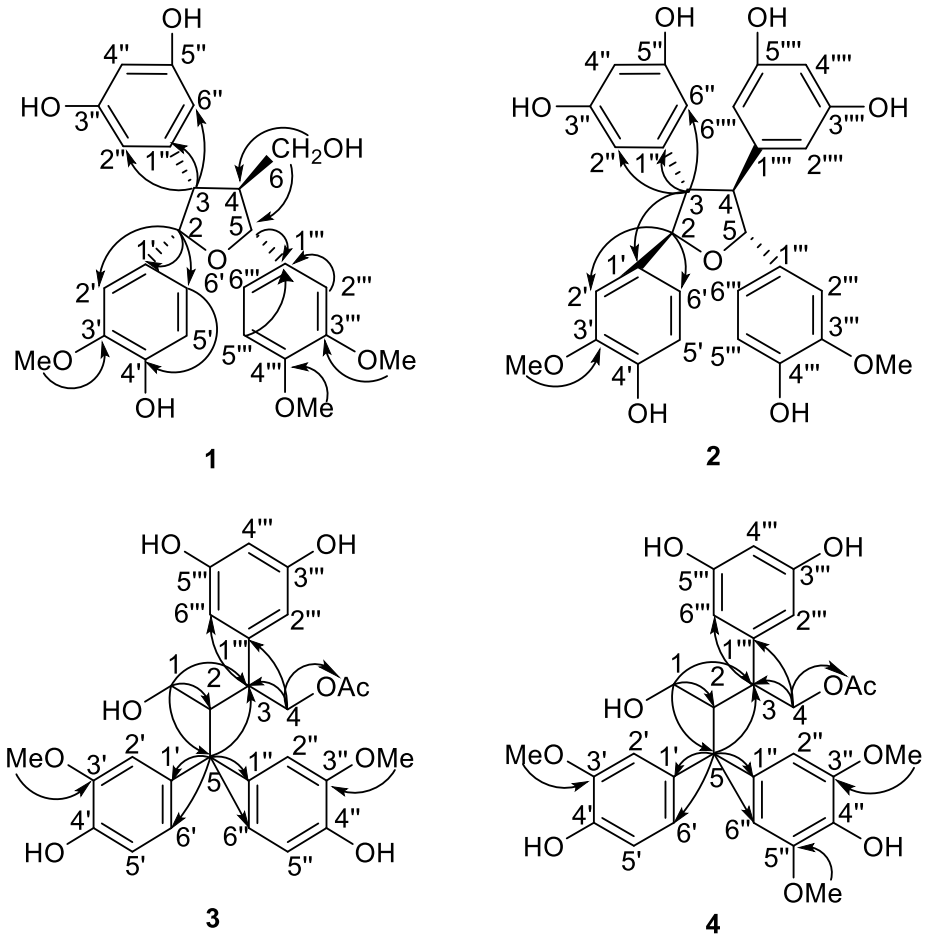

Figure 2. Selected HMBC correlations (H→C) of compounds **1-4**

δ_C 158.9 (C-3″, 5″, 3‴″, 5‴″), 148.3 (C-4′, 4‴), 146.6 (C-3′, 3‴), 141.1(C-1″, 1‴″), 133.9 (C-1′, 1‴), 119.4 (C-6′, 6‴), 115.5 (C-5′, 5‴), 110.4 (C-2′, 2‴), 107.3 (C-2″, 6″, 2‴″, 6‴″), 101.8 (C-4″, 4‴″), two tertiary methyl carbon signals at δ_C 88.6 (C-2, 5), 63.3 (C-3, 4) and one methoxy group signal at δ_C 55.8 (3′, 3‴-OMe).

Furthermore, comparing the molecular formula $C_{30}H_{28}O_9$ and 17 degrees of unsaturation of compound **2** with its fewer ^{1}H NMR and ^{13}C NMR signals, it indicated that this molecule had symmetrical elements and overlapping carbon signals with four phenyl rings and the integration of hydrogen in the ^{1}H NMR spectrum should be doubled. Thus, compound **2** had four phenyl rings which accounted for 16 units of the 17 degrees of unsaturation and the molecule was pentacyclic. Moreover, the ^{1}H NMR, ^{13}C NMR and HSQC spectra revealed four methines signals at δ_H 3.44 (2H, dd, J = 6.5, 3.0 Hz, H-3, 4) with δ_C 63.3 (C-3, 4) and δ_H 5.22 (2H, dd, J = 6.5, 3.0 Hz, H-2, 5) with δ_C 88.6 (C-2, 5), which suggested the presence of a tetrahydrofuran ring with symmetry substituents. From the above-mentioned analysis and HMBC correlations (Figure 2), it suggested that the four phenyl groups were linked to the four carbons of

tetrahydrofuran ring, respectively. It showed **2** was similar to compound **1** and had a symmetrical structure. Confirming evidence was obtained from the HMBC correlations of H-2, 5 with C-3, 4, C-2′, 2‴, C-6′, 6‴ and H-3, 4 with C-1′, 1‴, C-1″, 1⁗, C-2″, 6″, 2⁗, 6⁗. The location of the methoxy group at C-3′, 3‴ were proved by HMBC correlation between methoxy protons (δ_H 3.80) and C-3′, 3‴ (δc 146.6) and NOESY interactions of methoxy protons with H-2′, 2‴. The relative *trans* configuration between the methine protons at C-2, 5 and C-3, 4 were established by the weak interactions between H-2, 5 and H-3, 4 in the 1D and 2D NOESY spectra. Moreover, its basic skeleton is similar to the known (2*S*,3*R*,4*R*,5*S*)-2,3,4,5-tetrakis(4-methoxyphenyl)tetrahydrofuran[16] and tricuspidatol-A.[17] The ^{1}H NMR data of former compound showed the tetrahydrofuran signals at δ_H 5.26 (2H, dd, J = 6.3, 2.7 Hz) and 3.52 (2H, dd, J = 6.3, 2.7 Hz), while the data of tricuspidatol-A at δ_H 5.25 (2H, dd, J=5.0, 1.5 Hz) and 3.50 (2H, dd, J=5.0, 1.5 Hz), which both resemble the data of compound **2**. Thus, on the basis of 2D NOESY of **2**, we confirmed the relative stereochemistry structures of **2** in Figure 1. Consequently, the structure of **2**, named pouzolignan K, was characterized as 2,5-bis(4-hydroxy-3-methoxyphenyl)-3,4-bis(3,5-dihydroxyphenyl)tetrahydrofuran.

Compound **3** was obtained as white powder, the molecular formula of $C_{27}H_{30}O_9$ was determined from the HR-ESI-TOF-MS ($[M+Na]^+$, *m/z* 521.1786), suggesting 13 degrees of unsaturation. The UV spectrum showed absorption maxima at 275 and 281 nm in methanol, and the IR spectrum showed absorption bands at 3362, 1720, 1601, 1512 and 1462 cm^{-1}, indicating the presence of hydroxy group, carbonyl group, and aromatic ring. The ^{1}H NMR and ^{13}C NMR spectrum of **3** (Table 2) along with analysis of the DEPT spectra displayed 27 carbon signals and 30 proton signals. In the ^{1}H-NMR spectrum of **3** (Table 2), two 1, 3, 4-trisubstituted protons (ABX system) at δ_H 6.94 (1H, d, J = 2.0 Hz, H-2′), 6.90 (1H, dd, J = 2.0, 8.0 Hz, H-6'), 6.82 (1H, d, J = 8.0 Hz, H-5′), and 6.76 (1H, d, J = 2.0 Hz, H-2″), 6.65 (1H, dd, J = 8.0, 2.0 Hz, H-6″), 6.63 (1H, d, J = 8.0 Hz, H-5″), one 1, 3, 5-trisubstituted phenyl protons (AB_2 system) at δ_H 6.17 (2H, d, J = 2.0 Hz, H-2‴, 6‴), 6.19 (1H, t, J = 2.0 Hz, H-4‴), three methine protons at δ_H 2.84-2.88 (1H, m, H-2), 3.13-3.17 (1H, m, H-3), 3.37 (1H, d, J=12.0 Hz, H-5), two oxymethylene protons at δ_H 3.31-3.37 (2H, m, H-1), 4.51-4.59 (2H, m, H-4), two methoxyl protons at δ_H 3.90, 3.78 (each 3H, s), as well as an acetyl methyl protons at δ_H 1.94 (3H, s) were recognized. DEPT experiment revealed that **3** had ten quaternary carbons, twelve tertiary carbons, two methylenes and three methyl groups (Table 2). In the HMBC spectrum, correlations of H-5 (δ_H 3.37) with C-1′ (δ_C 137.9), C-6′ (δ_C 121.9), C-1″ (δ_C 137.3), and C-6″ (δ_C 121.1), proved that the two 1, 3, 4-trisubstituted phenyl rings were both linked to C-5.

Table 2. NMR spectral data for compounds **3, 4** and pouzolignan F

(in CD_3OD, δ in ppm, J in Hz. 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR)

position	**3**		**4**		pouzolignan F[a]	
	δc	δ_H	δc	δ_H	δc	δ_H
1	63.2	3.31-3.37 (2H, m)	63.2	3.28-3.35 (2H, m)	65.6	3.72 (1H, dd, 11.5, 4.5) 4.05 (1H, dd, 11.5, 4.0)
2	46.7	2.84-2.88 (1H, m)	46.7	2.82-2.89 (1H, m)	42.3	3.12-3.14 (1H, m)
3	46.5	3.13-3.17 (1H, m)	46.5	3.16-3.19 (1H, m)	48.9	3.01-3.04 (1H, m)
4	69.7	4.51-4.59 (2H, m)	69.7	4.53-4.72 (2H, m)	65.6	3.96-3.98 (1H, m) 3.84 (1H, d, 7.5)
5	53.2	3.37 (1H, d, 12.0)	53.7	3.36 (1H, d, 12.0)	53.5	3.65 (1H, d, 12.0)
1′	137.9		137.1		137.1	
2′	113.4	6.94 (1H, d, 2.0)	113.5	6.96 (1H, d, 2.0)	113.2	7.05 (1H, d, 2.0)
3′	149.3		149.3		149.3	
4′	146.0		146.1		146.0	
5′	116.6	6.82 (1H, d, 8.0)	116.6	6.83 (1H, d, 8.0)	116.2	6.82 (1H, d, 8.0)
6′	121.9	6.90 (1H, dd, 8.0, 2.0)	121.9	6.92 (1H, dd, 8.0, 2.0)	122.1	6.95 (1H, dd, 8.0, 2.0)
1″	137.3		137.2		136.7	
2″	112.4	6.76 (1H, d, 2.0)	105.9	6.48 (1H, s)	112.7	6.84 (1H, d , 2.0)
3″	149.0		149.4		148.9	
4″	145.8		134.9		145.8	
5″	116.3	6.63 (1H, d, 8.0)	149.4		116.2	6.65 (1H, d, 8.0)
6″	121.1	6.65 (1H, dd, 8.0, 2.0)	105.9	6.48 (1H, s)	121.5	6.70 (1H, dd, 8.0, 2.0)
1‴	142.4		142.4		142.9	
2‴, 6‴	109.5	6.17 (2H, d, 2.0)	109.5	6.18 (2H, d, 2.0)	109.1	6.10 (2H, d, 2.0)
3‴,5‴	159.3		159.3		159.3	
4‴	102.3	6.19 (1H, t, 2.0)	102.3	6.19 (1H, t, 2.0)	102.2	6.19 (1H, t, 2.0)

3′-OMe	56.7	3.90 (3H, s)	56.7	3.90 (3H, s)	56.6	3.92 (3H, s)
3″-OMe	56.5	3.78 (3H, s)	56.9	3.79 (3H, s)	56.5	3.80 (3H, s)
5″-OMe			56.9	3.79 (3H, s)		
Ac	21.1	1.94 (3H, s)	21.1	1.94 (3H, s)	20.6	1.87 (3H, s)
	173.2		173.2		172.8	

[a] data from 11.

Furthermore, H-3 (δ_H 3.13-3.17) with C-2‴, 6‴ (δ_C 109.5) indicated that the 1, 3, 5-trisubstituted phenyl ring was attached to C-3 as well (Figure 2).

The NMR data suggested that compound **3** had the uniform norligan skeleton as pouzolignan F[11] which was reported in our earlier phytochemical investigations. Comparing the NMR data of **3** with those of pouzolignan F, C-4 (δ_C 69.7) was shifted downfield 4.1 ppm and C-3 (δ_C 46.5) was shifted upfield 2.4 ppm, as well as correlations between H-4 with C-1‴, C-3, CH_3CO in HMBC, thus, the acetoxy group was attached to C-4. The position of the hydroxy and methoxy groups in compound **3** were established by extensive analysis of the HMBC spectra (Figure 2). Based on the above results, the structure of **3**, named pouzolignan L, was estabolished as 1-hydroxy-3-(3,5-dihydroxyphenyl)-2-[bis(4-hydroxy-3-methoxyphenyl)methyl]butyl acetate.

Compound **4** was obtained as white powder, the molecular formula of $C_{28}H_{32}O_{10}$ was assigned from the HR-ESI-TOF-MS ($[M+Na]^+$, *m/z* 551.1889), suggesting 13 degrees of unsaturation. The ^1H and ^{13}C NMR spectral data of **4** (Table 2) were similar to those of **3**, except for the presence of an additional methoxy group at δ_H 3.79 (3H, s) and δ_C 56.9, and the 1, 3, 4, 5-tetrasubstituted phenyl signals at δ_H 6.48 (2H, s, H-2″, 6″) with δ_C 105.9 (C-2″, 6″). The location of the methoxy group at C-5″ was confirmed by the HMBC correlation (Figure 2). Hence, the structure of **4,** named pouzolignan M, was identified as 1-hydroxy-3-(3,5-dihydroxyphenyl)-2-[4-hydroxy-3-methoxyphenyl-(4-hydroxy-3,5-dimethoxy-phenyl)]butyl acetate.

The known compounds were identified as rhamnocitrin (**5**), rhamnetin (**6**),[18] isorhamnetin (**7**)[19] and quercetin (**8**),[20] by comparing the spectroscopic data with those reported in the literature values.

EXPERIMENTAL

General UV spectra were obtained using a Shimadzu UV-2450 spectrophotometer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. NMR spectra were run on a Bruker AVANCE Ⅲ 500

spectrometer with TMS as internal standard, and the chemical shifts (δ) were expressed in ppm. HR-ESI-TOF-MS was performed on an API QSTAR time-of-flight spectrometer. TLC was performed on precoated silica gel GF254 plates from Yantai Jiangyou Company. Silica gel 100-200, 200-300 and 300-400 mesh from Qingdao Haiyang Chemical Company, YWG-C_{18} (50-70 μm) from Tianjin Boruijianhe Chromatography Technology Company and Sephadex LH-20 from Amersham Biosciences were used for column chromatography. Preparative RP-C_{18} HPLC was performed by a Shimazu LC-6AD series instrument with Shim-Park RP-C_{18} column (20×200 mm i.d.).

Plant material The aerial parts of *P. zeylanica* var. *microphylla* were collected in Guangzhou, Guangdong province of China on January, 2012 and identified by Professor Ji-Zhu Liu, Guangdong Pharmaceutical University. A voucher specimen (No. 20120113) has been deposited in the Lab of Traditional Chinese Medicine Chemistry, Guangdong Pharmaceutical University.

Extraction and Isolation The air-dried and powdered aerial parts of *P. zeylanica* var. *microphylla* (5 kg) were extracted with petroleum ether (150 L) under reflux for two times (1 h per time). After the solvent on the plants was volatized completely, the plants were extracted with EtOAc (150 L) under reflux for three times (1.5 h per time), which was evaporated under reduced pressure to yield a residue (80 g). The EtOAc extract was subjected to silica gel (100-200 mesh) column chromatography, eluted with petroleum ether-EtOAc (50:1→1:1), EtOAc, CH_2Cl_2-MeOH (1:1), MeOH to yield six fractions, Fr.A-F. Fr.D (13.4 g) was resubjected by silica gel (200-300 mesh) column chromatography, eluted with $CHCl_3$-MeOH (50:1→5:1) to yield Fr.D1-D5. Fr.D1 was separated by Sephadex LH-20, eluted with $CHCl_3$-MeOH (1:1) and purified by RP-C_{18} column (50-70 μm), using 70% MeOH as the eluent to afford **2** (7.5 mg). Fr.D2 was subjected to sephadex LH-20, eluted with $CHCl_3$-MeOH (1:1) to yield four fractions, and the second fraction (0.3 g) was purified by RP-C_{18} column (50-70 μm), eluted with 70% MeOH to afford **1** (17 mg). Fr.E (4 g) was resubjected to silica gel (200-300 mesh) column chromatography, eluted with CH_2Cl_2-MeOH (25:1→8:1) to yield Fr.E1-E4. Fr.E2 was separated repeatedly by silica gel (300-400 mesh) column chromatography, eluted with CH_2Cl_2-MeOH (17:1) and finally by preparative RP-C_{18} HPLC, eluted with MeOH-H_2O-HCO_2H (23:1:0.5) to afford **3** (14 mg). Fr.E3 was further fractionated repeately by silica gel (300-400 mesh) column chromatography, eluted with CH_2Cl_2-MeOH (14:1), then was separated by Sephadex LH-20, eluted with $CHCl_3$-MeOH (3:2) to afford **4** (14 mg). Fr.F (14 g) was

submitted to silica gel (200-300 mesh) column chromatography, eluted with $CHCl_3$-MeOH (20:1→1:1) to afford Fr.F1-F6. Fr.F2 (0.5 g), Fr.F4 (1.0 g) and Fr.F5 (0.3 g) were subjected to Sephadex LH-20, eluted with MeOH to yield compounds **5** (15 mg), **6** (15 mg), **7** (18 mg) and **8** (25 mg), respectively.

Pouzolignan D (1) : Brown amorphous powder; $[\alpha]_D^{20}$+34.0 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3360, 2940, 2840, 1608, 1520, 1455, 1347, 1270, 1150, 820 cm^{-1}; UV (MeOH) λ_{max} nm (log ε) 274 (4.02); HR-ESI-TOF-MS *m/z* 467.1729 $[M-H]^-$ (calcd 467.1733 for $C_{26}H_{27}O_8^-$), ^1H and ^{13}C NMR data (see Table 1).

Pouzolignan K (2): Brown tabular crystals ($CHCl_3$-MeOH 1:1); $[\alpha]_D^{20}$+71.4 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3351, 1605, 1516, 1459, 1435, 1273, 1238, 1156, 1124, 1031, 1001 and 921 cm^{-1}; UV (MeOH) λ_{max} nm (log ε) 280 (4.13); HR-ESI-TOF-MS *m/z* 555.1608 $[M+Na]^+$, 531.1740 $[M-H]^-$ (calcd 555.1611 for $C_{30}H_{28}NaO_9^+$, 531.1743 for $C_{30}H_{27}O_9^-$), ^1H and ^{13}C NMR data (see Table 1).

Pouzolignan L (3): white powder; $[\alpha]_D^{20}$+29.7 (*c* 0.1, MeOH); UV (MeOH) λ_{max} nm (log ε) 275 (3.25); IR (KBr) ν_{max} 3362, 2942, 1720, 1601, 1512, 1462, 1365, 1128 and 849 cm^{-1}, HR-ESI-TOF-MS *m/z* 521.1786 $[M+Na]^+$ (calcd 521.1788 for $C_{27}H_{30}NaO_9^+$), ^1H and ^{13}C NMR data (see Table 2).

Pouzolignan M (4): white powder; $[\alpha]_D^{20}$+36.1 (*c* 0.1, MeOH), UV (MeOH) λ_{max} nm (log ε) 275(3.34); IR (KBr) ν_{max} 3362, 2941, 1721, 1602, 1514, 1462, 1366, 1126 and 849 cm^{-1}; HR-ESI-TOF-MS *m/z* 551.1889 $[M+Na]^+$ (calcd 551.1893 for $C_{28}H_{32}NaO_{10}^+$) ^1H and ^{13}C NMR data (see Table 2).

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