Rhyncosides A—F, Phenolic Constituents from the Chinese Mangrove Plant *Bruguiera sexangula* var. *rhynchopetala*

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Chemical investigation on the stem of a Chinese mangrove plant *Bruguiera sexangula* var. *rhynchopetala* (Rhizophoraceae) resulted in the isolation and characterization of four new phenolic glycosides rhyncosides A—D (1—4), and two new lignan derivatives namely rhyncosides E—F (5—6), along with twelve known phenolic constituents. Their structures were determined by extensive spectroscopic data analyses.

Key words *Bruguiera sexangula* var. *rhynchopetala*; phenolic glycoside; lignan derivative; spectroscopic data

The genus *Bruguiera* (Rhizophoraceae) represents evergreen trees widely distributed in tropical Africa, Australia, and South and Southeast Asia, as well as in the tropical Pacific.[1)] Previous chemical investigation mainly focused on *B. gymnorrhiza*, *B. sexangula*, and *B. cylindrical*, showing a variety of tropane derivatives,[1—3)] aromatic compounds (bruguierols A—C),[4)] diterpenes,[5—8)] triterpenes,[9)] benzoquinones,[10)] flavonoids,[11)] unique dithiolans,[12—14)] and polydisulfide.[15)] *Bruguiera sexangula* var. *rhynchopetala* is an endemic species distributed in coast line of South China. Our previous examination of this plant resulted in the isolation of diterpenes and disulfides.[5)] A continuous investigation for chemical diversity of *B. sexangula* var. *rhynchopetala* led the isolation and characterization of six new phenolic constituents named rhyncosides A—F (**1**—**6**) (Fig. 1), together with twelve known compounds including two phenolic glycosides, four flavonoids, and six lignan derivatives. The structures have been established by 1D and 2D NMR including COSY, HSQC, HMBC (Fig. 2) spectroscopic data analyses, and by comparison with those reported in literature.

Results and Discussion

A repeated chromatography on *n*-BuOH fraction from EtOH extract of stem of *B. sexangula* var. *rhynchopetala* afforded eighteen compounds including six new phenolic compounds (**1**—**6**), (Fig. 1).

Rhyncoside A (**1**) was obtained as a white amorphous powder, and its molecular formula was designated as $C_{18}H_{26}O_{12}$ from the negative HR-FAB-MS (*m*/*z* 433.1350 $[M-H]^-$, Calcd 433.1351), indicating six degrees of unsaturation. The IR absorptions suggested the presence of hydroxy (3419 cm^{-1}), and aromatic functions (1652, 1513 cm^{-1}). The ^{1}H-NMR spectrum exhibited the resonances at δ 3.74 (3H, s) for a methoxy group, δ 4.67 (1H, d, J=7.5 Hz) and 4.73 (1H, br s) for two anomeric protons, δ 6.66 (1H, d, J=8.6 Hz), 6.64 (1H, d, J=2.3 Hz), and 6.47 (1H, dd, J=2.3, 8.6 Hz) for

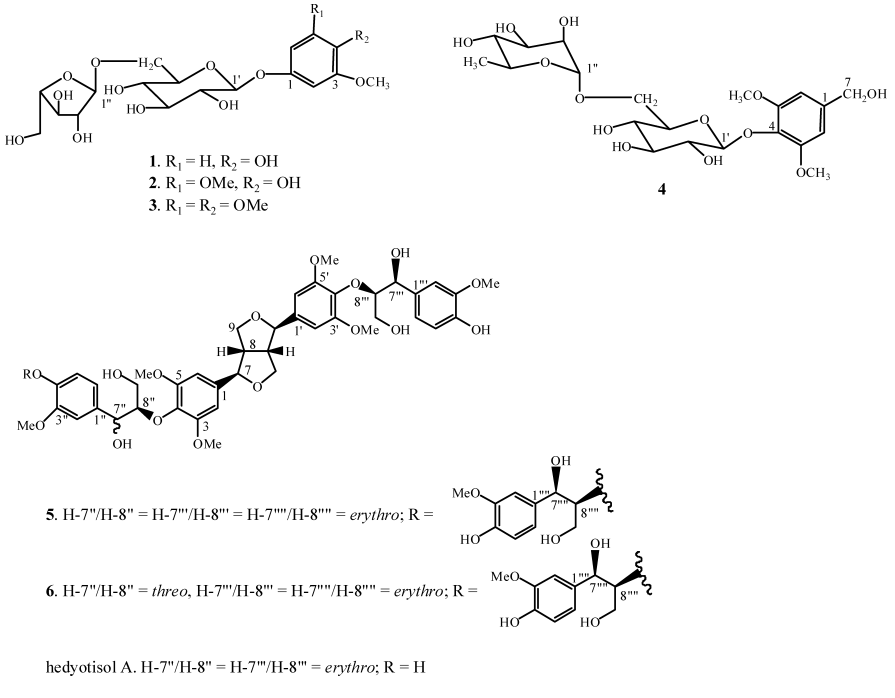

Fig. 1. Structures of Compounds **1**—**6**

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Table 1. The ^{1}H- and ^{13}C-NMR Data of Rhyncosides A—D (**1**—**4**)[a)]

Position	**1**		**2**		**3**		**4**	
1		151.1 (s)		150.3 (s)		155.2 (s)		139.0 (s)
2	6.64 (d, 2.3)	102.8 (d)	6.33 (s)	94.9 (d)	6.36 (s)	95.4 (d)	6.62 (s)	104.8 (d)
3		148.3 (s)		148.3 (s)		154.4 (s)		153.1 (s)
4		141.8 (s)		130.4 (s)		133.7 (s)		133.5 (s)
5	6.66 (d, 8.6)	115.8 (d)		148.3 (s)		154.4 (s)		153.1 (s)
6	6.47 (dd, 2.3, 8.6)	108.4 (d)	6.33 (s)	94.9 (d)	6.36 (s)	95.4 (d)	6.62 (s)	104.8 (d)
7							4.42 (d, 4.8)	63.5 (t)
Glc								
1′	4.67 (d, 7.5)	102.0 (d)	4.71 (d, 8.5)	101.5 (d)	4.75 (d, 8.5)	102.0 (d)	4.71 (d, 7.1)	103.6 (d)
2′	3.19 (m)	73.7 (d)	3.17 (m)	73.7 (d)	3.24 (m)	74.4 (d)	3.18 (m)	74.5 (d)
3′	3.25 (m)	77.0 (d)	3.25 (m)	76.6 (d)	3.30 (m)	77.7 (d)	3.17 (m)	76.9 (d)
4′	3.07 (m)	70.7 (d)	3.05 (m)	70.4 (d)	3.09 (m)	71.5 (d)	3.05 (m)	70.5 (d)
5′	3.47 (m)	75.8 (d)	3.50 (m)	75.5 (d)	3.43 (m)	76.7 (d)	3.17 (m)	76.1 (d)
6′	3.38 (dd, 10.6, 3.6)	67.7 (t)	3.38 (m)	67.3 (t)	3.37 (m)	68.4 (t)	3.33 (m)	67.1 (t)
	3.92 (d, 10.6)		3.94 (d, 10.5)		3.97 (d, 10.2)		3.70 (d, 11.1)	
		Ara		Ara		Ara		Rhm
1″	4.73 (br s)	108.9 (d)	4.73 (br s)	108.4 (d)	4.75 (br s)	109.6 (d)	4.46 (br s)	101.1 (d)
2″	3.79 (m)	82.6 (d)	3.75 (m)	82.3 (d)	3.75 (m)	83.4 (d)	3.48 (m)	70.8 (d)
3″	3.64 (m)	77.6 (d)	3.63 (m)	77.3 (d)	3.60 (m)	78.5 (d)	3.35 (m)	71.1 (d)
4″	3.74 (m)	84.3 (d)	3.70 (m)	83.9 (d)	3.74 (m)	85.1 (d)	3.18 (m)	72.4 (d)
5″	3.55 (m)	61.8 (t)	3.36 (m)	61.4 (t)	3.30 (m)	62.6 (t)	3.06 (m)	68.7 (d)
	3.41 (m)		3.56 (m)		3.55 (m)			
6″							1.07 (d, 6.0)	18.3 (q)
3-OMe	3.74 (s)	56.0 (q)	3.74 (s)	56.0 (q)	3.76 (s)	57.1 (q)	3.74 (s)	56.7 (q)
4-OMe					3.60 (s)	61.4 (q)		
5-OMe			3.74 (s)	56.0 (q)	3.76 (s)	57.1 (q)	3.74 (s)	56.7 (q)
4-OH	8.56 (s)		7.89 (s)					
7-OH							5.20 (t, 4.8)	

a) Measured in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C, δ in ppm, J in Hz).

an ABX system of an aromatic ring, and multiplets corresponding to $H_{2—6}$ of sugar moieties in the range of δ 3.0—4.8 ppm. The ^{13}C-NMR and DEPT spectra displayed eighteen carbon resonances involving six aromatic carbons at δ 151.1 (s), 102.8 (d), 148.3 (s), 141.8 (s), 115.8 (d), and 108.4 (d), a methoxy group at 56.0 (q), and eleven carbons around δ 60—110 ppm which were attributable to sugar moieties (Table 1). The DQFCOSY, HMQC and HMBC data (Fig. 2) revealed the signals at δ 102.0 (d, C-1′), 73.7 (d, C-2′), 77.0 (d, C-3′), 70.7 (d, C-4′), 75.8 (d, C-5′), and 67.7 (t, C-6′) to be agreement with a 1,6-disubstituted glucopyranose, while the signals at δ 108.9 (d, C-1″), 82.6 (d, C-2″), 77.6 (d, C″), 84.3 (d, C-4″), and 61.8 (t, C-5″) were consistent with a C-1 substituted arabinofuranose.[16,17] The linkage of sugar moieties was determined to be 1→6 connection according to the HMBC correlation between an anomeric proton (δ 4.73, br s, H-1″) and C-6″, and in turn between H_2-6′ (δ 3.38, 3.92,) and C-1″. In addition, the HMBC correlation from the other anomeric proton at δ 4.67 (d, H-1′) to C-1 (δ 151.1, s) indicated that C-1′ of glucose linked to C-1 of aromatic ring through an ether bond. A hydroxy and a methoxy groups were determined to be at C-4 and C-3 respectively as the HMBC correlation from the phenolic proton at δ 8.56 (s) to C-4 (δ 141.8, s) and C-5 (δ 115.8, d) was observed. The J value of H-1′ (7.5 Hz) indicated a β-configuration of glucopyranose, whereas the ^{1}H- and ^{13}C-NMR data were in agreement with a α-configuration of arabinofuranose. The absolute configurations of sugars were assumed to be L-arabinofuranose and D-glucose on the basis of their biogenetically related to compound **3**, in which the sugar configuration was determined by GLC comparison with authentic sugars. Accordingly, the structure of **1** was established as 1-*O*-[α-L-arabinofuranosyl-(1→6)-β-D-glucopyranosyl]-3-methoxy-4-hydroxyphenol.

Rhyncoside B (**2**) was obtained as a white amorphous powder. The negative HR-FAB-MS gave an ion peak at m/z 463.1466 $[M-H]^-$ (Calcd for 463.1457), corresponding to a molecular formula of $C_{19}H_{28}O_{13}$. The IR absorptions at 3424 and 1649 cm^{-1} suggested the presence of hydroxy and aromatic groups. The ^{1}H- and ^{13}C-NMR data of **2** were very similar with those of **1**, with exception of the signals for aromatic ring, where the presence of two equivalent aromatic protons at δ 6.33 (2H, s) and two methoxy groups at δ 3.74 (6H, s), indicating a symmetrical substitution of the aromatic ring. A phenolic proton at δ 7.89 (s) showed HMBC correlations with δ 130.4 (s, C-4) and 148.3 (s, C-3, C-5), indicating the presence of a 4-hydroxy-3,5-dimethoxyphenol unit. The linkage between arabinofuranose and glucopyranose was determined to be the same as described in compound **1**. The connection of C-1′ of glucopyranose to C-1 of aromatic ring was based on the HMBC correlation between H-1′ (δ 4.71, d, J=8.5 Hz) and C-1 (δ 150.3, s). The structure of **2** was thus determined as 1-*O*-[α-L-arabinofuranosyl-(1→6)-β-D-glucopyranosyl]-4-hydroxy-3,5-dimethoxyphenol.

Rhyncoside C (**3**) was obtained as a white amorphous powder. Its molecular formula of $C_{20}H_{30}O_{13}$ was determined by a negative HR-FAB-MS (m/z 477.1610 $[M-H]^-$, Calcd 477.1613), with 14 amu more than that of **2**. The IR, ^{1}H- and ^{13}C-NMR data of **3** showed very similarity with those of **2**, except for presence of an additional methoxy group (δ 3.60, s; 61.4, q) instead of a hydroxy group of **2**. The HMBC correlations from the methoxy protons and the aromatic protons at δ 6.36 (2H, s) to δ 133.7 (s, C-4) enabled the assignment of a 3,4,5-trimethoxyphenol unit. The linkage of aromatic

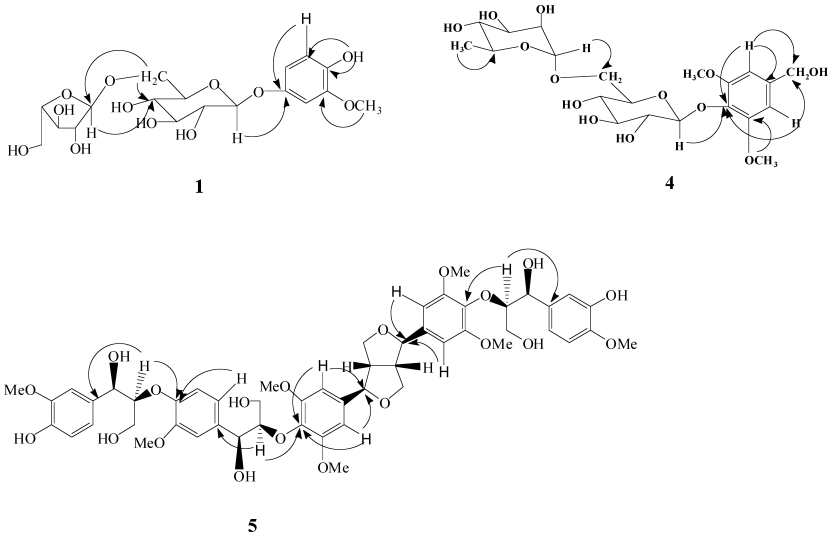

Fig. 2. Key HMBC Correlations of **1**, **4**, and **5**

ring and sugar units was in agreement with that of **1**. The sugar configuration was confirmed to be L-arabinofuranose and D-glucose according to GLC data. Therefore, the structure of **3** was identified as 1-*O*-[α-L-arabinofuranosyl-(1→6)-β-D-glucopyranosyl]-3,4,5-trimethoxyphenol.

Rhyncoside D (**4**) was obtained as a white amorphous powder. Its molecular formula of $C_{21}H_{32}O_{13}$ was determined by negative HR-FAB-MS (*m/z* 491.1769 $[M-H]^-$, Calcd 491.1770). The IR spectrum exhibited absorptions at 3422, 1655, 1487 cm^{-1}, which are characteristic of hydroxy and aromatic groups. The ^{1}H-NMR data indicated the presence of two methoxy groups at δ 3.74 (6H, s), a methyl group at δ 1.07 (3H, d, J=6.0 Hz), an oxymethylene group at δ 4.42 (2H, d, J=4.8 Hz), two anomeric protons at δ 4.71 (1H, d, J=7.1 Hz) and 4.46 (1H, br s), two aromatic protons at δ 6.62 (2H, s), and multiplets corresponding to sugar moieties in the range of δ 3.0—4.8 ppm. The ^{1}H- and ^{13}C-NMR spectral data of **4** were partially related to those of 3,5-dimethoxy-4-hydroxybenzyl alcohol 4-*O*-β-D-glucopyranoside,[18,19] with the exception of the additional ^{13}C resonances at δ 101.1 (d), 70.8 (d), 71.1 (d), 72.4 (d) , 68.7 (d), 18.3 (q) for a L-rhamnopyranose unit. The rhamnosyl moiety was connected to C-6′ (δ 67.1, t) of glucopyranose through (1→6)-linkage on the basis of the downfield shifted C-6′ and the HMBC correlation between anomeric proton at δ 4.46 (1H, br s, H-1″) and C-6′ (Fig. 2). The presence of four carbons (δ 153.1, 139.0, 133.5, 104.8) in aglycone suggested a symmetrical substitution of aromatic ring. Two overlapping protons at δ 6.62 (2H, s) showing HMBC correlations with δ 153.1 (s, C-3, C-5), 139.0 (s, C-1), 133.5 (s, C-4), 104.8 (d, C-2 or C-6)), and 63.5 (t, C-7), and the methoxy protons at δ 3.74 (6H, s) with C-3 and C-5 assigned the substitution of aglycone. The connection of sugar unit to C-4 rather than to C-7 was based on the HMBC interaction between H-1′ of glucose (δ 4.71, d, J=7.1 Hz) and C-4 of aromatic ring. Thus, a hydroxymethylene should be substituted at C-1 of aromatic ring (Fig. 2). The J values of anomeric protons in glucopyranose and rhamnopyranose were indicative of β- and α-configurations, respectively. The sugar configuration was confirmed to be D-glucose and L-rhamnopyranose according to GLC data. The structure of **4** was thus determined as 4-*O*-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-1-hydroxymethyl-3,5-dimethoxybenzene.

The molecular formula of rhyncoside (**5**) was determined as $C_{52}H_{62}O_{20}$ by negative HR-FAB-MS (*m/z* 1005.3751 $[M-H]^-$, Calcd 1005.3761) and NMR data. The IR absorptions at 3427, 1634, 1594, 1510, 1029, and 1003 cm^{-1} suggested the presence of hydroxy, phenyl and ether groups. The ^{1}H-NMR spectrum of **5** exhibited the signals at δ 6.65 (4H, s, H-2, 2′, 6, 6′) for two symmetrical 1,3,4,5-tetra-substituted aromatic rings, the methoxy signals at δ 3.76 (12H, s) for four equivalent methoxy groups, and the proton signals at δ 4.67 (2H, br s, H-7,7′), 3.07 (2H, m, H-8, 8′), 3.83 (2H, br d, J=9.0 Hz, H-9a, 9a′), and 4.20 (2H, dd, J=7.0, 9.0 Hz, H-9b, 9b′) for a *bis*-tetrahydrofuran ring. Those data in association with ^{13}C-NMR data were indicative of a furofuran lignan nucleus, closely related to syringaresinol.[20] Furthermore, three ABX phenyl systems resonated at δ 6.92 (1H, d, J=1.5 Hz, H-2″), 6.69 (1H, d, J=8.0 Hz, H-5″), 6.71 (1H, dd, J=1.5, 8.0 Hz, H-6″), 6.98 (1H, d, J=1.7 Hz, H-2‴), 6.69 (1H, d, J=7.6 Hz, H-5‴), 6.71 (1H, dd, J=1.7, 7.6 Hz, H-6‴), 6.99 (1H, d, J=1.5 Hz, H-2⁗), 6.96 (1H, d, J=8.0 Hz, H-5⁗), and 6.81 (1H, dd, J=1.5, 8.0 Hz, H-6⁗) were observed in ^{1}H-NMR spectrum. The proton corresponding carbons were assigned by HMQC spectrum. With the exception of carbon resonances assignable to syringaresinol nucleus and the signals for three additional aromatic rings (Table 2). The ^{13}C-NMR and DEPT spectra of **5** exhibited three hydroxymethylenes at δ 60.2 (t, C-9″), 60.3 (t, C-9‴), and 60.5 (t, C-9⁗), and six oxygenated methines at δ 86.6 (d, C-8″, C-8‴), 84.4 (d, C-8⁗), 72.5 (d, C-7″), 72.6 (d, C-7‴), and 72.1 (d, C-7⁗). Those NMR data clearly indicated that **5** possessed three arylglycerol moieties. A comparison of NMR data revealed that partial structure of **5** closely resembled hedyotisol A,[21] a furofuran dilignan derivative originated from *Hedyotis lawsoniae*. The difference was due to the presence of an additional guaiacylglycerol moiety, which was deduced to C-4″ through a C-8⁗/C-4″ β-guaiacyl ether bond according to the HMBC correlations from δ 4.28 (1H, m, H-8⁗) and 6.71 (dd, H-6″) to δ 145.8 (s, C-4″), (Fig. 2).

The relative stereochemistry of **5** could be determined by NOE data and by comparison NMR data with those of

Table 2. ^{1}H- and ^{13}C-NMR Data of Rhyncosides E, F (**5**, **6**)[a] and Hedyotisol A[b]

Position	Hedyotisol A		**5**			**6**		
	δ_C	δ_H	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC
1, 1′	137.7 (s)		137.3 (s)			137.3 (s)		
2, 2′, 6, 6′	102.9 (d)	6.61 (s)	103.7 (d)	6.65 (s)	C-4, 4′, C-7, 7′	103.8 (d)	6.65 (s)	C-4, 4′, C-7, 7′
3, 3′, 5, 5′	153.6 (s)		153.1 (s)			153.1 (s)		
4, 4′	134.4 (s)		135.3 (s)			137.4 (s)		
7, 7′	86.0 (d)	4.77 (br s)	85.6 (d)	4.67 (br s)	C-2, 2′, C-6, 6′, C-8, 8′, C-9, 9′	85.5 (d)	4.67 (br s)	C-2, 2′, C-6, 6′, C-8, 8′, C-9, 9′
8, 8′	54.6 (d)	3.12 (m)	54.2 (d)	3.07 (m)	C-1, 1′, C-7, 7′, C-9, 9′	54.2 (d)	3.07 (m)	C-1, 1′, C-7, 7′, C-9, 9′
9, 9′	72.1 (t)	3.95 (br d, 9.3)	71.8 (t)	3.83 (br d, 9.0)	C-8,8′, C-7,7′	71.8 (t)	3.82 (br d, 9.0)	C-8, 8′, C-7, 7′
		4.33 (m)		4.20 (dd, 7.0, 9.0)			4.21 (dd, 6.5, 9.0)	
1″	131.3 (s)		133.8 (s)			133.8 (s)		
2″	108.4 (d)	6.74 (d, 1.5)	111.3 (d)	6.92 (d, 1.5)	C-4″, C-6″, C-7″	111.4 (d)	6.93 (d, 2.0)	C-4″, C-6″, C-7″
3″	146.7 (s)		147.4 (s)			147.5 (s)		
4″	145.0 (s)		145.8 (s)			145.8 (s)		
5″	114.3 (d)	6.83 (d, 8.5)	115.1 (d)	6.69 (d, 8.0)	C-1″, C-3″, C-4″	115.1 (d)	6.70 (d, 8.0)	C-1″, C-3″, C-4″
6″	118.9 (d)	6.71 (br d, 1.5, 8.5)	119.8 (d)	6.71 (dd, 1.5, 8.0)	C-1″, C-3″, C-4″	119.8 (d)	6.71 (dd, 2.0, 8.0)	C-1″, C-3″, C-4″
7″	72.6 (d)	4.97 (d, 4.5)	72.5 (d)	4.80 (m)	C-2″, C-6″, C-8″, C-9″	71.4 (d)	4.80 (m)	C-2″, C-6″, C-8″, C-9″
8″	87.2 (d)	4.10 (m)	86.6 (d)	4.10 (m)	C-4, C-1″, C-7″, C-9″	87.4 (d)	4.11 (m)	C-4, C-1″, C-7″, C-9″
9″	60.7 (t)	3.47 (m)	60.2 (t)	3.40 (m)	C-7″, C-8″	60.3 (t)	3.41 (m)	C-7″, C-8″
		3.85 (m)						
1‴	131.3 (s)		133.4 (s)			135.8 (s)		
2‴	108.4 (d)	6.74 (d, 1.5)	111.6 (d)	6.98 (d, 1.7)	C-4‴, C-6‴, C-7‴	111.5 (d)	7.00 (d, 2.0)	C-4‴, C-6‴, C-7‴
3‴	146.7 (s)		145.9 (s)			147.6 (s)		
4‴	145.0 (s)		147.6 (s)			145.9 (s)		
5‴	114.3 (d)	6.83 (d, 8.5)	115.1 (d)	6.69 (d, 7.6)	C-1‴, C-3‴, C-4‴	115.1 (d)	6.70 (d, 8.0)	C-1‴, C-3‴, C-4‴
6‴	118.9 (d)	6.71 (br d, 1.5, 8.5)	119.4 (d)	6.71 (dd, 1.7, 7.6)	C-2‴, C-3‴, C-4‴, C-7‴	120.0 (d)	6.72 (dd, 2.0, 8.0)	C-2‴, C-3‴, C-4‴, C-7‴
7‴	72.6 (d)	4.97 (d, 4.5)	72.6 (d)	4.83 (m)	C-2‴, C-6‴, C-8‴, C-9‴′	72.6 (d)	4.88 (m)	C-2‴, C-6‴, C-8‴, C-9″
8‴	87.2 (d)	4.10 (m)	86.6 (d)	4.10 (m)	C-4′, C-1‴, C-7‴, C-9‴	86.6 (d)	4.00 (m)	C-4′, C-1‴, C-7‴, C-9‴
9‴	60.7 (t)	3.47 (m)	60.3 (t)	3.74 (m)	C-7‴, C-8‴	60.6 (t)	3.15 (m)	C-7‴, C-8‴
		3.85 (m)					3.60 (m)	
C-1⁗			135.8 (s)			133.4 (s)		
2⁗			111.8 (d)	6.99 (d, 1.5)	C-4⁗, C-6⁗, C-7⁗	111.9 (d)	7.00 (d, 1.8)	C-4⁗, C-6⁗, C-7⁗
3⁗			149.6 (s)			149.4 (s)		
4⁗			147.3 (s)			147.3 (s)		
5⁗			115.6 (d)	6.96 (d, 8.0)	C-1⁗, C-3⁗, C-4⁗	115.6 (d)	6.90 (d, 8.0)	C-1⁗, C-3⁗, C-4⁗
6⁗			119.6 (d)	6.81 (dd, 1.5, 8.0)	C-2⁗, C-4⁗, C-7⁗	119.5 (d)	6.89 (dd, 1.8, 8.0)	C-2⁗, C-4⁗, C-7⁗
7⁗			72.1 (d)	4.72 (m)	C-2⁗, C-6⁗, C-8⁗, C-9⁗	72.1 (d)	4.72 (m)	C-2⁗, C-6⁗, C-8⁗, C-9⁗
8⁗			84.4 (d)	4.28 (m)	C-4″, C-1⁗, C-7⁗, C-9⁗	84.4 (d)	4.23 (m)	C-4″, C-1⁗, C-7⁗, C-9⁗
9⁗			60.5 (t)	3.57 (m)	C-7⁗, C-8⁗	60.6 (t)	3.19 (m)	C-7⁗, C-8⁗
				3.60 (m)			3.60 (m)	
MeO-3, 3′, 5, 5′	56.4 (q)	3.88 (s)	56.5 (q)	3.76 (s)	C-3, 3′, 5, 5′	56.5 (s)	3.76 (s)	C-3, 3′, 5, 5′
MeO-3″	56.1 (q)	3.89 (s)	55.9 (q)	3.74 (s)	C-3″	56.1 (q)	3.74 (s)	C-3″
MeO-3‴	56.1 (q)	2.89 (s)	56.1 (q)	3.75 (s)	C-3‴	56.0 (q)	3.75 (s)	C-3‴
MeO-3⁗			55.9 (q)	3.74 (s)	C-3⁗	55.9 (q)	3.74 (s)	C-3⁗

a) Measured in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C, δ in ppm, J in Hz); *b*) measured in $CDCl_3$.

known arylglycerol derivatives.[22] A strong NOESY correlation between δ 6.65 (4H, s, H-2,2′,6,6′) and 3.07 (2H, H-8,8′) suggested the β-orientation of H-8 and H-8′ and in turn the α-orientation of H-7 and H-7′. The stereochemical assignment of side chains of arylglycerols could be followed by comparison of their ^{13}C values with those of similar structural pattern as concluded by Unge.[22] The ^{13}C data of C-7″/C-8″ (72.5/86.6) and C-7‴/C-8‴ (72.6/86.6) were in agreement with *erythro*-forms of arylglycerol β-syringyl ethers, while C-7⁗/C-8⁗ (72.1/84.4) was also designed to *erythro* arylglycerol β-guaiacyl ether.[22] Accordingly, the structure of **5** was determined as *erythro*-4″-*O*-guaiacylhedyotisol A.

The HR-FAB-MS data of rhyncoside F (**6**) showed the same molecular formula as that of **5**. A 2D NMR analysis and comparison of IR, NMR data clarified that the gross structure of **6** was identical to **5**. The Cα/Cβ data (C-7″/C-8″, 71.4/87.4) of arylglycerol β-syringyl ether (left side) was in agreement with *threo*, whereas the Cα/Cβ data (C-7‴/C-8‴, 72.6/86.6) for arylglycerol β-syringyl ether at right side was assignable to *erythro* form. The Cα/Cβ data of arylglycerol β-guaiacyl ether appeared at 72.1/84.4 (C-7⁗/C-8⁗) was indicative of *erythro* form.[22]

The known phenolic compounds were classified to two phenolic glycosides (3,4,5-trimethoxyphenyl-β-D-glucopyranoside[23] and 1-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]-3,4,5-trimethoxybenzene,[24]) four flavonoids (tricin, rutin,[25] nicotiflorin, and myricetin-3-*O*-rutinoside[26]), and six lignans (lyoniside,[27] (+)-lyoniresinol-3α-*O*-α-L-rhamnopyranoside,[28] (+)-5′-methoxyisolariciresinol-9′-β-D-xylopyranoside,[29] and hedyotisols A—C[21]), and their structures were identified by comparison of spectroscopic data with those in literature. All of the known compounds were isolated from mangrove plants for the first time.

Experimental

General Procedure Optical rotations were measured on a PERKIN-ELMER 243B polarimeter. IR spectra were determined on a Thermo Nicolet Nexus 470 FT-IR spectrometer. HR-FAB-MS were obtained on a Bruker Daltonics. Inc. APEX II. FT-ICRMS spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance-500 FT NMR spectrometer. Chemical shifts are expressed in δ (ppm) and coupling constants are reported in Hz. Column chromatography was carried out with silica gel (200—300 mesh) and GF254 silica gel for TLC were provided by Qingdao Marine Chemistry Co., Ltd., Qingdao, China. D-101 macroporous resin was provided by Haiguang Chemistry Co., Ltd., Tianjin, China, while polyamide (60—90 mesh) was supplied by Linjiang Chemistry Co., Ltd., Jiangsu, China. Sephadex LH-20 (18—110 μm) was obtained from Pharmacia. HPLC was performed on an Alltech 426 apparatus using a Kromasil prepack column (ODS, 10 mm×250 mm, for reversed phase). The GLC spectra were detected on HP5890A-VG20-250 GC-MS instrument (VG Co.), and the data were detected on VG11-250 data system.

Plant Material The specimen of *B. sexangula* var. *rhynchopetala* was collected at the coastline closed to Xiamen, Fujian Province, China, in July 2002. The species was identified by Prof. Lin Peng, Xia Men University. A voucher specimen (M-011) was deposited at the State Key Laboratory of Natural and Biomimetic Drugs, Peking University.

Extraction and Isolation The stems (4.9 kg) were air-dried and then grounded. The powdered sample was extracted with 95% EtOH twice at room temperature and then extracted with hot 95% EtOH at 60 °C for 3 h (three times). Both extracts were combined and concentrated in vacuum to afford a brown residue (218 g). The residue was suspended in water and then partitioned successively with petroleum ether, EtOAc and BuOH. The *n*-BuOH fraction (66 g) was subjected to a column of a macro-porous resin and was washed with H_2O firstly, and followed by a gradient of EtOH–H_2O. The 10% EtOH fraction (5.0 g) was separated by silica gel column eluting with $CHCl_3$–MeOH (10 : 1—5 : 1) to afford 3,4,5-trimethoxyphenyl-β-D-glucopyranoside (80 mg), and a mixture containing **3** and **6**. This mixture (210 mg) was purified by HPLC (ODS, 20% MeOH–H_2O) to give **3** (110 mg) and 1-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]-3,4,5-trimethoxybenzene (3.0 mg). The 20% EtOH fraction (1.1 g) was separated by silica gel column eluting with $CHCl_3$–MeOH (7 : 1) and then purified by HPLC (ODS, 30% MeOH–H_2O) to give lyoniside (27 mg), (+)-lyoniresinol-3α-*O*-α-L-rhamnopyranoside (8.0 mg), and (+)-5′-methoxyisolariciresinol-9′-β-D-xylopyranoside (10 mg). The fractions from 50% EtOH to EtOH eluents were combined according to the TLC. The combined fraction (3.4 g) was subjected to polyamide column eluting with H_2O and a gradient EtOH–H_2O. The H_2O fraction (150 mg) was separated by silica gel column eluting with $CHCl_3$–MeOH (5 : 1) to afford a mixture mainly containing **1** and **2**, which was separated by semi-preparative HPLC (ODS, 15% MeOH–H_2O) to give **1** (20 mg), **2** (9.0 mg), and **4** (2.3 mg). The remaining fractions from polyamide column were combined and then subjected to silica gel column eluting with $CHCl_3$–MeOH–H_2O (25 : 8 : 1) to collect two portions which were detected by TLC. The first portion (150 mg) was purified by Sephadex LH-20 eluting with 80% MeOH–H_2O to afford rutin (33.2 mg), tricin (4.5 mg), nicotiflorin (7.1 mg), myricetin-3-*O*-rutinoside (3.5 mg), while the second portion (98 mg) was separated by semi-preparative HPLC (C-18) with 60% MeOH–H_2O as mobile phase to obtain **5** (5.1 mg) and **6** (4.7 mg), hedyotisols A (4.5 mg), B (5.1 mg), and C (2.0 mg).

A solution of **3** (10 mg) in 1 N HCl (dioxane–H_2O, 1 : 1, 2 ml) was heated at 90 °C for 2 h. After the precipitate was removed by filtration, the supernatant was extracted with EtOAc (2 ml×3). The H_2O layer was neutralized by passing through an Amberlite IRA-400 column and concentrated to yield a monosaccharide residue. The residue was dissolved in pyridine (0.2 ml), to which L-cysteine methyl ester hydrochloride in pyridine (0.2 mg/ml) was added and then heated at 60 °C for 1 h. After the reaction mixture was dried *in vacuo*, the residue was trimethylsilylated with 1-trimethylsilyimidazole (TMS, 0.2 ml) and then heated at 60 °C for additional 40 min. The mixture was partitioned between *n*-hexane/H_2O to collect *n*-hexane extract. The *n*-hexane extract was analyzed by GC-MS under the following conditions: capillary column (OV-1, 0.32 mm×30 m), column temperature (230 °C), detection temperature (270 °C), injection temperature (270 °C), carrier gas (He, 2.2 kg/cm^2). Compound **4** (1.2 mg) was performed by the same method. The derivatives of standard monosaccharides of D-glucose, L-glucose, L-rhamnose, L-arabinose, and D-arabinose were prepared and detected by the similar way, which showed retention times of 17.02 (D-glucose), 17.11 (L-glucose), 8.23 (L-rhamnose), 9.75 (L-arabinose), and 9.53 (D-arabinose) min, respectively. The monosaccharides of **1** were in agreement with D-glucose and L-arabinose, while the monosaccharides of **4** were identical to D-glucose and L-rhamnose.

Rhyncosides A (**1**): White amorphous powder, $[\alpha]_D^{20}$ −42.4° (c=1.99, H_2O). IR (KBr) ν_{max}: 3419, 1652, 1513, 1053, 1027, 1004 cm^{-1}. ^{1}H- and ^{13}C-NMR (DMSO-d_6) data, see Table 1. HR-FAB-MS *m*/*z*: 433.1350 [M−H]$^-$ (Calcd for $C_{18}H_{25}O_{12}$, 433.1351).

Rhyncosides B (**2**): White amorphous powder, $[\alpha]_D^{20}$ −8.2° (c=0.33, H_2O). IR (KBr) ν_{max}: 3424, 1649, 1049, 1027, 1004 cm^{-1}. ^{1}H- and ^{13}C-NMR data, see Table 1. HR-FAB-MS *m*/*z*: 463.1466 [M−H]$^-$ (Calcd for $C_{19}H_{27}O_{13}$, 463.1457).

Rhyncosides C (**3**): White amorphous powder, $[\alpha]_D^{20}$ −53.8° (c=2.41, H_2O); IR (KBr) ν_{max}: 3385, 2927, 1601, 1505, 1128, 1026 cm^{-1}. ^{1}H- and ^{13}C-NMR data, see Table 1. HR-FAB-MS *m*/*z*: 477.1610 [M−H]$^-$ (Calcd for $C_{20}H_{29}O_{13}$, 477.1613).

Rhyncosides D (**4**): White amorphous powder, $[\alpha]_D^{20}$ −10.1° (c=0.40, H_2O). IR (KBr) ν_{max}: 3422, 1655, 1487, 1154, 1049, 1026 cm^{-1}. ^{1}H- and ^{13}C-NMR data, see Table 1. HR-FAB-MS *m*/*z*: 491.1769 [M−H]$^-$ (Calcd for $C_{21}H_{31}O_{13}$, 491.1770).

Rhyncosides E (**5**): Pale yellow gum. IR (KBr) ν_{max}: 3427, 2929, 1634, 1594, 1510, 1125, 1029, 1003 cm^{-1}. ^{1}H- and ^{13}C-NMR data, see Table 2. FAB-MS *m*/*z*: 1045 [M+K]$^+$, 1029 [M+Na]$^+$, 1007 [M+H]$^+$. HR-FAB-MS *m*/*z*: 1005.3751 [M−H]$^-$ (Calcd for $C_{52}H_{61}O_{20}$, 1005.3761).

Rhyncosides F (**6**): Pale yellow gum. IR (KBr) ν_{max}: 3424, 2927, 1634, 1506, 1126, 1029, 1003 cm^{-1}. ^{1}H- and ^{13}C-NMR data, see Table 2. FAB-MS *m*/*z*: 1045 [M+K]$^+$, 1029 [M+Na]$^+$, 1007 [M+1]$^+$. HR-FAB-MS *m*/*z*: 1005.3767 [M−H]$^-$ (Calcd for $C_{52}H_{61}O_{20}$, 1005.3761).

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