Litseaglutinan A and Lignans from *Litsea glutinosa*

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A new abscisic acid derivative, named litseaglutinan A (**1**), and a new arylnaphthalene-type lignan, (7′*S*,8*R*,8′*S*)-4,4′,9-trihydroxy-3,3′,5-trimethoxy-9′-*O*-*β*-D-xylopyranosyl-2,7′-cyclolignan (**2**), were isolated from the AcOEt extract of *Litsea glutinosa*, together with nine known lignans. Their structures were established by spectroscopic methods.

Introduction. – Plants of the genus *Litsea* (Lauraceae) are distributed widely in tropical and subtropical parts of Asia, North America, and subtropical South America [1]. *Litsea glutinosa* (LOUR.) C. B. ROB., an evergreen arbor, is mainly distributed in the provinces of Guangdong, Guangxi, Fujiang, and Yunnan of China. Its bark and leaves are used as traditional medicine for the treatment of diarrhoea and dysentery [1]. Alkaloids, flavonoids, and aromatic compounds were reported from *L. glutinosa* [1–5]. In the continuing search for potential drug leads from the genus *Litsea*, two new compounds, *i.e.*, an abscisic acid derivative, named litseaglutinan A (**1**), and an arylnaphthalene lignan, named (7′*S*,8*R*,8′*S*)-3,3′,5-trimethoxy-4,4′,9-trihydroxy-9′-*O*-*β*-D-xylopyranosyl-2,7′-cyclolignan (**2**), were isolated from the stems of *L. glutinosa*, together with nine known lignans (*Fig. 1*). Their structures were elucidated by spectroscopic methods, including HSQC, HMBC, NOESY, and ^{1}H,^{1}H-DQF-COSY. The relative and absolute configurations of these compounds were determined by NOE and circular dichroism (CD) spectra, and biogenetic consideration. In addition, antibacterial activities of some lignans against *Bacillus subtilis*, *B. thuringiensis*, and *Staphylococcus aureus* were evaluated.

Results and Discussion. – Compound **1** was obtained as a light-yellow amorphous powder. The molecular formula, $C_{29}H_{38}O_{14}$, was established by HR-ESI-MS (*m*/*z* 609.2205 ([*M* – H]$^-$; calc. 609.2183)). On the basis of the ^{1}H- and ^{13}C-NMR data (*Table 1*), and the HSQC, HMBC, NOESY, and ^{1}H,^{1}H-DQF-COSY correlations, the structure of **1** was established as 3-hydroxy-4,5-dimethoxyphenyl 6-*O*-{(2*E*,4*E*)-5-[(1*R*,3*S*,5*S*,8*S*)-3,8-dihydroxy-1,5-dimethyl-7-oxo-6-oxabicyclo[3.2.1]oct-8-yl]-3-methylpenta-2,4-dienoyl}-*β*-D-glucopyranoside, named litseaglutinan A.

The positive reaction of **1** with $FeCl_3$/EtOH solution and its UV absorption maximum at λ_{max} 266 nm indicated the presence of a phenol unit in **1**. The DEPT experiments showed that **1** had two MeO, three Me, three CH_2, and six O-bearing CH

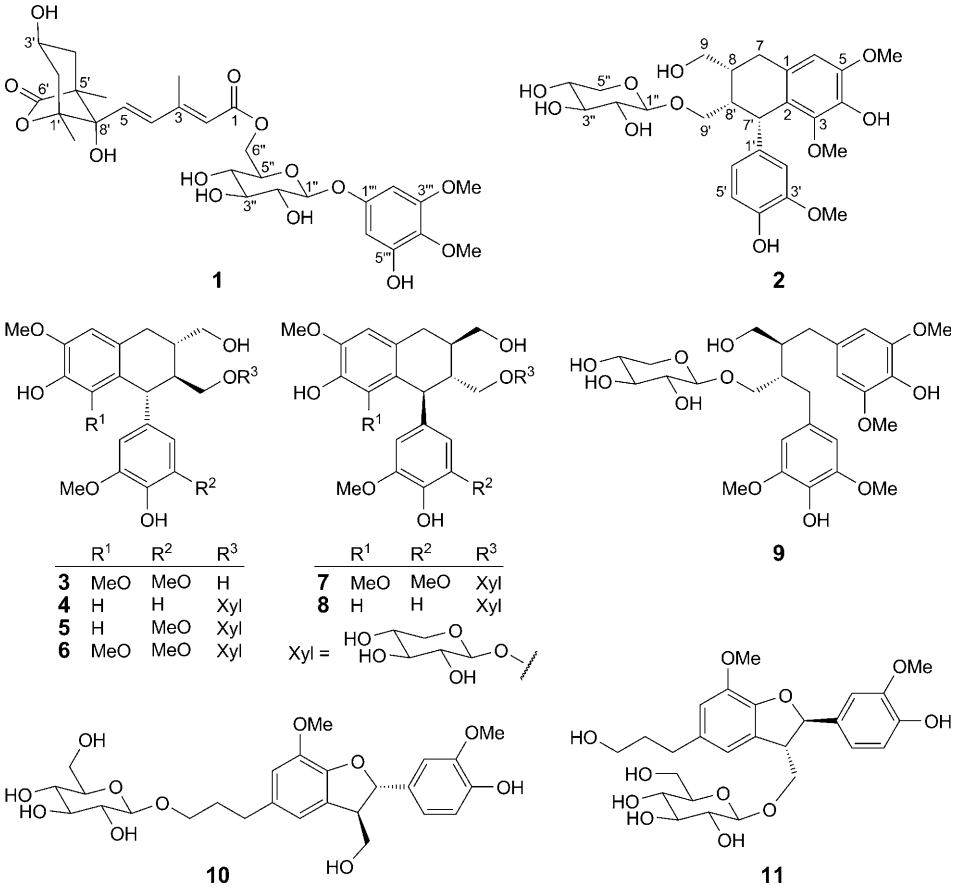

Fig. 1. *Structures of compounds* **1**–**11**

groups, and ten quaternary C-atoms (including two C=O groups). The NMR data showed that compound **1** comprise a phenolic ring, a glucopyranose unit, and a sesquiterpene moiety. The resonances of two aromatic H-atoms at δ(H) 6.28 (*d*, $J = 2.1$, H–C(6‴)) and 6.29 (*d*, $J = 2.1$ Hz, H–C(2‴)), and of the corresponding C-atoms at δ(C) 98.9 (C(6‴)) and 95.1 (C(2‴)), along with four O-bearing aromatic C-atom signals at δ(C) 155.7 (C(1‴)), 154.8 (C(3‴)), 133.1 (C(4‴)), and 151.7 (C(5‴)), suggested the presence of a 1,3,4,5-tetrasubstituted benzene ring. HMBCs from the H-atom signals of two MeO groups at δ(H) 3.81 (*s*) and 3.74 (*s*) to those of C(3‴) and C(4‴), respectively, suggested the substitution pattern shown in *Fig. 2*. The presence of a glucopyranose unit was indicated by NMR data, HMBC, and ^{1}H,^{1}H-DQF-COSY spectrum. The HMBC from the anomeric H-atom at δ(H) 4.78 (*d*, $J = 7.3$, H–C(1″)) to C(1‴) revealed the C(1″)–O–C(1‴) linkage between this β-D-glucopyranose unit and the benzene ring. The NMR data for the partial structure of the glycosylated benzene ring were in good agreement with those of thorelinin [6]. However, the NMR data of the sesquiterpene moiety in **1** are different from those in thorelinin. The presence of an

Table 1. *^{13}C- and ^{1}H-NMR Data* (at 125 and 500 MHz, resp., in CD_3OD) *of Compound* **1**. δ in ppm, J in Hz.

	δ(C)	δ(H)		δ(C)	δ(H)
C(1)	167.3		H–C(3″)	77.9	3.45–3.49 (*m*)
H–C(2)	119.4	5.92 (*s*)	H–C(4″)	71.8	3.39 (*dd*, *J* = 9.3, 8.7)
C(3)	151.9		H–C(5″)	75.5	3.67 (*ddd*, *J* = 8.7, 7.0, 2.0)
H–C(4)	133.4	8.04 (*d*, *J* = 15.9)	CH_2(6″)	64.4	4.50 (*dd*, *J* = 11.8, 2.0),
H–C(5)	132.8	6.49 (*d*, *J* = 15.9)	C(1‴)	155.7	4.32 (*dd*, *J* = 11.8, 7.0)
C(1′)	89.9		H–C(2‴)	95.1	6.29 (*d*, *J* = 2.1)
CH_2(2′)	42.3	2.27 (*dd*, *J* = 14.3, 6.9, H_{ax}),	C(3‴)	154.8	
		1.85 (*dd*, *J* = 14.3, 10.1, H_{eq})	C(4‴)	133.1	
H–C(3′)	65.2	3.83–3.88 (*m*)	C(5‴)	151.7	
CH_2(4′)	41.0	1.92 (*dd*, *J* = 13.6, 6.8, H_{ax}),	H–C(6‴)	98.9	6.28 (*d*, *J* = 2.1)
		1.74 (*dd*, *J* = 13.6, 11.1, H_{eq})	*Me*–C(3)	21.1	2.14 (*s*)
C(5′)	53.5		*Me*–C(1′)	18.5	1.34 (*s*)
C(6′)	181.0		*Me*–C(5′)	14.6	1.09 (*s*)
C(8′)	82.9		*Me*O–C(3‴)	56.5	3.81 (*s*)
H–C(1″)	102.9	4.78 (*d*, *J* = 7.3)	*Me*O–C(4‴)	61.2	3.74 (*s*)
H–C(2″)	74.9	3.42–3.45 (*m*)			

ester C(6′)=O was suggested by its C-atom chemical shift at δ(C) 181.0. It was indicated that this ester group was derived through the oxidization of a CH_2 group in the bicyclic sesquiterpene moiety of thorelinin. Hence, the sesquiterpene moiety was identified as (2*E*,4*E*)-5-[(1*R**,3*S**,5*S**,8*S**)-3,8-dihydroxy-1,5-dimethyl-7-oxo-6-oxabicyclo[3.2.1]oct-8-yl]-3-methylpenta-2,4-dienoic acid [7]. The upfield shift of the ester C(1)=O C-atom in **1** and the HMBC from CH_2(6″) to C(1) suggested the linkage of the sesquiterpene and sugar moiety *via* an ester bond.

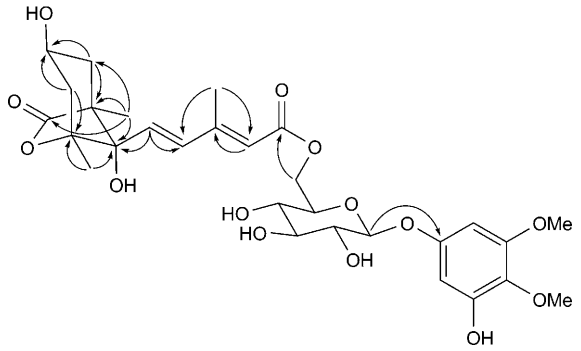

Fig. 2. *Selected HMBCs* (H → C) *of compound* **1**

In the NOESY spectrum, correlations H_{ax}–C(2′)/H–C(5), Me(1′)/H–C(5), H_{ax}–C(4′)/H–C(5), Me(5′)/H–C(5), H_{ax}–C(2′)/H_{ax}–C(4′), H–C(3′)/H_{eq}–C(4′), and H_{eq}–C(2′)/H_{eq}–C(4′) were observed, establishing the relative configuration of **1** as shown in *Fig. 3*. Since the sesquiterpene moiety of **1** was regarded as a derivative of abscisic acid, which is a growth hormone in plants, the absolute configurations at C(1′),

C(5′), and C(8′) in **1** were deduced by biogenetic considerations to be (*R*), (*S*), and (*S*), respectively [8]. On the basis of the above results, the structure of the aglycon of compound **1** was determined as (2*E*,4*E*)-5-[(1*R*,3*S*,5*S*,8*S*)-3,8-dihydroxy-1,5-dimethyl-7-oxo-6-oxabicyclo[3.2.1]oct-8-yl]-3-methylpenta-2,4-dienoate.

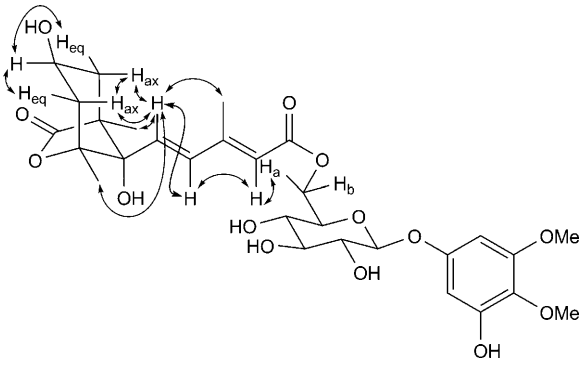

Fig. 3. *Selected NOE correlatons* (H ↔ H) *of compound* **1**

Compound **2** was obtained as a light yellow amorphous powder, $[\alpha]_D^{22} = +13.9^\circ$ ($c =$ 0.1, MeOH). The molecular formula, $C_{26}H_{34}O_{11}$, was established by the HR-ESI-MS (*m*/*z* 545.1990 ($[M+Na]^+$; calc. 545.1999) and 561.1732 ($[M+K]^+$; calc. 561.1738)). The ^{1}H- and ^{13}C-NMR data (*Table 1*), and HSQC, HMBC, NOESY, and ^{1}H,^{1}H-DQF-COSY correlations established the structure of **2** as (7′*S*,8*R*,8′*S*)-4,4′,9-trihydroxy-3,3′,5-trimethoxy-9′-*O*-*β*-D-xylopyranosyl-2,7′-cyclolignan, a new arylnaphthalene type lignan.

The DEPT experiment indicated the presence of three MeO, four CH_2, and eleven CH groups, and eight quaternary C-atoms in **2**. A positive reaction with $FeCl_3$/EtOH solution and its UV maximum absorption at 284 nm suggested the presence of phenolic units in **2**. A typical aromatic *ABX* coupling system (*δ*(H) 6.64 (*d*, *J* = 8.0, 1 H); 6.50 (*dd*, *J* = 8.0, 1.2, 1 H); 6.75 (*d*, *J* = 1.2, 1 H)) in the ^{1}H-NMR spectrum revealed a 1,3,4-substituted benzene ring in this compound. The resonances of an aromatic H-atom (*δ*(H) 6.58 (*s*, 1 H)) and of six aromatic C-atoms (*δ*(C) 130.2 (C(1)), 126.7 (C(2)), 147.6 (C(3)), 139.0 (C(4)), 148.6 (C(5)), and 107.9 (C(6))) indicated another pentasubstitued benzene ring. Based on the HSQC and ^{1}H,^{1}H-DQF-COSY spectra, a partial structure of **2** was established as shown in *Fig. 4*, and the ^{1}H- and ^{13}C-NMR data were assigned as shown in *Table 2*. HMBCs from H−C(7′) to aromatic C-atoms C(1′), C(1), and C(2), together with those from CH_2(7) to C(1) and C(2), established a tetrahydronaphthalene lignan aglycone in compound **2** (*Fig. 5*). Moreover, the presence of a *β*-D-xylose unit was suggested by its ^{1}H- and ^{13}C-NMR data, and HMBC and ^{1}H,^{1}H-DQF-COSY spectra. The HMBC from the anomeric H-atom at *δ*(H) 4.23 (*d*, *J* = 7.50, H−C(1″)) to C(9′) indicated a C(1″)−O−C(9′) linkage between the *β*-D-xylose unit and aglycone. Furthermore, the attachments of three MeO groups (*δ*(H) 3.87 (*s*), 3.79 (*s*), and 3.29 (*s*)) to C(3), C(3′), and C(5), respectively, were disclosed according to the HMBC cross-peaks of MeO/C(3), MeO/C(3′), and MeO/C(5), respectively.

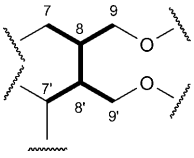

Fig. 4. *Partial structure of compound* **2** *and key* $^{1}H,^{1}H$*-DQF-COSY correlations* (—)

Table 2. ^{13}C- *and* ^{1}H*-NMR Data* (at 125 and 500 MHz, resp., in CD_3OD) *of Compound* **2**. δ in ppm, J in Hz.

	δ(C)	δ(H)		δ(C)	δ(H)
C(1)	130.2		H–C(5′)	115.8	6.64 (*d*, *J* = 8.0)
C(2)	126.7		H–C(6′)	121.8	6.50 (*dd*, *J* = 8.0, 1.2)
C(3)	147.6		H–C(7′)	42.9	4.37 (*d*, *J* = 6.4)
C(4)	139.0		H–C(8′)	46.9	2.06 (*m*)
C(5)	148.6		CH_2(9′)	71.2	3.47 (*dd*, *J* = 9.3, 5.1),
H–C(6)	107.9	6.58 (*s*)			3.41 (*dd*, *J* = 9.36, 4.2)
CH_2(7)	34.0	2.71 (*dd*, *J* = 15.2, 4.5, H_a),	H–C(1″)	105.5	4.23 (*d*, *J* = 7.5)
		2.60 (*dd*, *J* = 15.2, 11.8, H_b)	H–C(2″)	75.0	3.23 (*dd*, *J* = 8.2, 7.5)
H–C(8)	40.7	1.67–1.75 (*m*)	H–C(3″)	78.0	3.31–3.33 (*m*)
CH_2(9)	66.2	3.64 (*dd*, *J* = 10.8, 4.2),	H–C(4″)	71.3	3.83–3.86 (*m*)
		3.54 (*dd*, *J* = 10.8, 6.6)	H–C(5″)	67.0	3.80–3.83 (*m*),
C(1′)	140.2				3.17 (*dd*, *J* = 11.0, 10.8)
H–C(2′)	113.7	6.75 (*d*, *J* = 1.2)	*Me*O–C(5)	60.0	3.29 (*s*)
C(3′)	148.7		*Me*O–C(3)	56.7	3.87 (*s*)
C(4′)	145.4		*Me*O–C(3′)	56.6	3.79 (*s*)

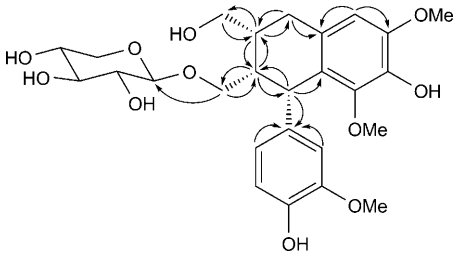

Fig. 5. *Selected HMBCs* (H → C) *of compound* **2**

The observed NOE correlations between H–C(7′)/H–C(8), H–C(8′)/H–C(8), and H–C(7′)/H–C(8′) indicated the relative configuration (7′*S**,8*R**,8′*S**) (*Fig. 6*). The CD spectrum of compound **2** showed *Cotton* effects at 226 ($\Delta\varepsilon = -8.24$), 243 ($\Delta\varepsilon = +9.14$), and 275 nm ($\Delta\varepsilon = +7.61$), which were consistent with those of the reported compound (6*R*,7*S*,8*S*)-7a-[(β-D-glucopyranosyl)oxy]-1-methoxyisolariciresinol [9]. Consequently, the absolute configuration of compound **2** was established to be (7′*S*,8*R*,8′*S*) (*Fig. 1*). On the basis of the above results, the structure of compound **2** was elucidated as (7′*S*,8*R*,8′*S*)-4,4′,9-trihydroxy-3,3′,5-trimethoxy-9′-*O*-β-D-xylopyranosyl-2,7′-cyclolignan.

The structures of other lignans **3**–**11** were identified by comparison of their NMR data with those reported in the literature. They were (–)-lyoniresinol (**3**) [10], (–)-isolariciresinol-9′-*O*-β-D-xylopyranoside (**4**) [11], (–)-isolariciresinol-5′-methoxy-9′-*O*-

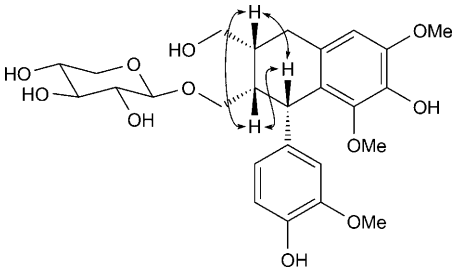

Fig. 6. *Selected NOE correlations* (H ↔ H) *of compound* **2**

β-D-xylopyranoside (**5**) [12], (7′*R*,8*S*,8′*R*)-nudiposide (**6**) [13], (7′*S*,8*R*,8′*S*)-lyoniresinol (**7**) [13], (7′*S*,8*R*,8′*R*)-4,4′,9-trihydroxy-3′,5-dimethyl-9′-*O*-β-D-xylopyranosyl-2,7′-cyclolignan (**8**) [14], ssioriside (**9**) [15], glochidioboside (**10**) [16], and [(2*R*,3*S*)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-5-(3-hydroxypropyl)-7-methoxy-1-benzofuran-3-yl]methyl β-D-glucopyranoside (**11**) [7]. In the previous studies, four types of lignans, *viz.*, ditetrahydrofuran, tetrahydrofuran, benzofuran, and biphenyl, were reported from plants of the *Litsea* genus. In this study, two more types *viz.* arylnaphthalene lignan, **2**–**8**, and dibenzylbutanelignan, **9**, were identified from *L. glutinosa*. The absolute configurations of these compounds were established according to their UV, NMR, OR, and CD data. In addition, compounds **10** and **11** were benzofuran-type lignans. Their configurations were ascribed by comparison of their OR data with those reported in the literature.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 100–200 and 200–300 mesh, *Qingdao Haiyang Chemical plant*, Qingdao, P. R. China). Semi-prep. HPLC: *Waters-600E* HPLC pump and *Waters-996* photodiode array detector, *ODS* column (250 × 4.6 mm and 250 × 10 mm, 5 μm, *YMC*). Optical rotations (OR): *Jasco P-1020* polarimeter. UV Spectra: *Varian-Cary-100* UV/VIS spectrophotometer; λ_{max} (log ε) in nm. CD Spectra: *Jasco J-810* CD spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: *Bruker AV-500* spectrometer at 500 (^{1}H) and 125 MHz (^{13}C), resp.; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS: *SCIEX API 2000* mass spectrometer; in *m*/*z* (rel. %). HR-EI-MS: *VG AutoSpec-3000* mass spectrometer; in *m*/*z* (rel. %).

Plant Material. Fresh stems of *L. glutinosa* were collected from Wenchang, Hainan Province, P. R. China, in December 2005. The plant was identified by *S. Z.*, South China Sea Institute of Oceanology, Chinese Academy of Sciences. A voucher specimen (No. LGPan06) was deposited with the Guangdong Provincial Key Laboratory of Marine Materia Medica, Guangzhou, P. R. China.

Extraction and Isolation. Fresh stems of *L. glutinosa* (10 kg) were extracted with EtOH at r.t. for three times. The combined extracts were evaporated under reduced pressure to yield a dark-brown extract (1.1 kg). The extract was suspended in H_2O (2.0 l) and then extracted successively with petroleum ether (4 × 3.0 l), AcOEt (5 × 3.0 l), and BuOH (5 × 3.0 l). The AcOEt extract (27.6 g) was subjected to CC over SiO_2 (100–200 mesh, petroleum ether/AcOEt 5 : 1 → 5 : 4 and then $CHCl_3$/MeOH 30 : 1 → 1 : 1) to afford 14 fractions, *Frs. 1–14*. *Fr. 11* (2.4 g) was further purified by CC (SiO_2; 200–300 mesh, $CHCl_3$/acetone 40 : 1 → 1 : 1) and gave six subfrations. The last subfraction was then purified by CC (SiO_2; 200–300 mesh, $CHCl_3$/MeOH 20 : 1 → 1 : 1) and afforded compound **5** (12 mg). *Fr. 14* (3.0 g) was pufied by CC (SiO_2; 200–300 mesh, $CHCl_3$/MeOH 40 : 1 → 1 : 1) and gave five subfrations. *Subfr. 3* was decolorized by *Sephadex LH-20* column eluted with MeOH and then purified by *RP-*C_{18} HPLC (MeOH/H_2O 20 : 80) to afford compound **2** (5.3 mg), **3** (4.9 mg), **4** (5.1 mg), and **9** (6.7 mg). *Subfr. 4* was decolorized by *Sephadex LH-20* column eluted with MeOH and purified by *RP-*C_{18} HPLC (MeOH/H_2O 19 : 81) to give

compound **1** (7.7 mg), **7** (5.8 mg), **8** (12.4 mg), **10** (10.5 mg), and **11** (4.2 mg). *Subfr. 6* was decolorized by *Sephadex LH-20* column eluted with MeOH and purified by *RP-C_{18}* HPLC (MeOH/H_2O 16:84) to afford compound **6** (7.4 mg).

Litseaglutinan A (= *3-Hydroxy-4,5-dimethoxyphenyl 6*-O-*{(2*E,*4*E*)-5-[(1*R,*3*S,*5*S,*8*S*)-3,8-Dihydroxy-1,5-dimethyl-7-oxo-6-oxabicyclo[3.2.1]oct-8-yl]-3-methylpenta-2,4-dienoyl}-β*-D-*glucopyranoside*; **1**). Light yellow amorphous powder. UV (MeOH): 202, 266. ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS: 633.3 ($[M+Na]^+$). HR-ESI-MS: 609.2205 ($[M-H]^-$, $C_{29}H_{37}O_{14}^-$; calc. 609.2183).

*(7′*S,*8*R,*8′*S*)-4,4′,9-Trihydroxy-3,3′,5-trimethoxy-9′*-O-*β*-D-*xylopyranosyl-2,7′-cyclolignan* (= *[(1*S,*2*S,*3*R*)-1,2,3,4-Tetrahydro-7-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-3-(hydroxymethyl)-6,8-dimethoxynaphthalen-2-yl]methyl β*-D-*Glucopyranoside*; **2**). Light yellow amorphous powder. $[\alpha]_D^{22} = +13.9$ ($c = 0.1$, MeOH). UV (MeOH): 238, 284. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS: 545.1990 ($[M+Na]^+$, $C_{26}H_{34}NaO_{11}^+$; calc. 545.1999), 561.1732 ($[M+K]^+$, $C_{26}H_{34}KO_{11}^+$; calc. 561.1738).

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