Xylocosides A – G, Phenolic Glucosides from the Stems of *Xylosma controversum*

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Seven new phenolic glucosides, xylocosides A – G (**1** – **7**), together with 18 known compounds were isolated from the stems of *Xylosma controversum* CLOS. In compounds **3** – **6**, the glucose residue is esterified at C(6) by 2-hydroxycyclopentanecarboxylic acid. These new structures were established by spectroscopic-data interpretation and chemical methods.

1. Introduction. – *Xylosma controversum* CLOS (Flacourtiaceae) is widespread in the south and southwest of China. It's roots and leaves, named 'Hongchuanposhi', are used as folk medicines in Guangxi province of China [1]. Up to now, there are only a few reports on the study of secondary metabolites of *Xylosma* genus, from which some benzoylated phenolic glucosides such as xylosmacin, xylosmin, and poliothyrsoside were isolated as the major constituents [2]. These types of phenolic glucosides have been widely found in the family Flacourtiaceae [3].

As part of our systematic study on Flacourtiaceae plants in China, searching for new bioactive products and chemotaxonomic markers [3], the stems of *X. controversum* were investigated. In a previous article, we reported the isolation of lignans, flavones, phenols, and (+)-(*R*)-chaulmoogric acid [2e], and in the present study, continued investigation led to the isolation and structural elucidation of seven new phenolic glucosides, xylocosides A – G (**1** – **7**; see *Fig. 1*), together with 18 known phenolic constituents. The structures of **1** – **7** were determined from the spectral data and chemical evidence. By comparison of their NMR data with those in literature, the known compounds were identified as 3-(4-hydroxy-3,5-dimethoxyphenyl)propane-1,2-diol (**8**) [4], pyrocatechol-1-*O*-β-apiofuranosyl-(1″ → 6′)-β-glucopyranoside [5], pyrocatechol-1-*O*-β-xylopyranosyl-(1″ → 6′)-β-glucopyranoside and pyrocatechol-1-*O*-β-glucopyranoside [6], catechol [7], 3,4,5-trimethoxyphenol-1-*O*-β-apiofuranolyl-(1″ → 6′)-β-glucopyranoside [8], 3,4,5-trimethoxyphenol-1-*O*-β-xylopyranosyl-(1″ → 6′)-β-glucopyranoside [9], 3,4,5-trimethoxyphenol-1-*O*-β-glucopyranoside, 3,4,5-trimethoxyphenol [10], junipetroloside A [11], *threo*-syringyl glycerol [12], *threo*-guaiacyl glycerol and *erythro*-guaiacyl glycerol [13], syringin [14], salirepin [15], tachioside, isotachioside [16], and the newly reported rhyncoside C [17].

2. Results and Discussion. – Compound **1** was obtained as an amorphous solid. Its molecular formula was assigned to be $C_{17}H_{26}O_{10}$ by the quasimolecular ion peak [*M* +

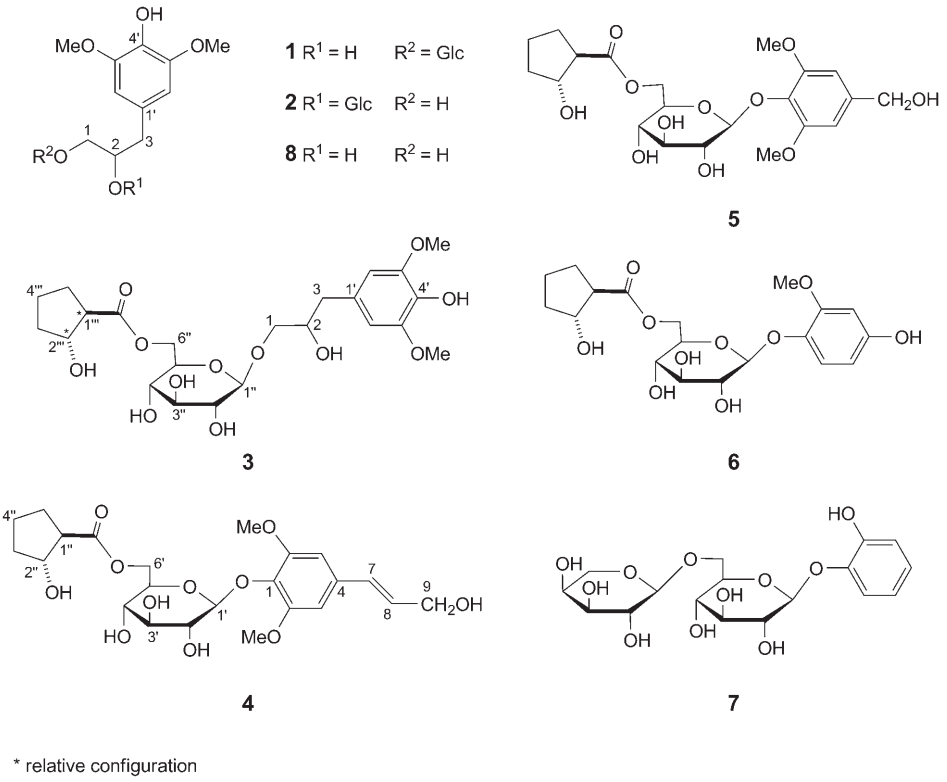

Fig. 1. *Structures of compounds* **1**–**8**

Na]$^+$ at *m*/*z* 413.1425 (calc. for $C_{17}H_{26}NaO_{10}^+$, 413.1424) in the HR-ESI-MS spectrum. In the ^{1}H- and ^{13}C-NMR data (*Table 1*), the ^{1}H-NMR signals of a β-glucose residue (δ(H) 4.27, *d*, $J = 8.0$, H–C(1″)), a 1,2,4,6-tetrasubstituted aromatic ring (δ(H) 6.54 (*s*, H–C(2′), H–C(6′)) and two MeO groups (δ(H) 3.83 (*s*, MeO–C(3′), MeO–C(5′))), together with ^{13}C-NMR signals of one CH_2 group (δ(C) 40.9), one CH_2O group (δ(C) 74.1), and one CHO group (δ(C) 72.7) suggested that **1** was a glucoside of **8** [4], which was further supported by HSQC and HMBC data. A downfield shift of C(1) (δ(C) 74.1) compared to the free CH_2–OH group in **8** at δ(C) 66.6 indicated that the glucose residue was attached at C(1), which was confirmed by the HMBC correlations from H–C(1″) to C(1). Therefore, compound **1** was identified as 2-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-1-yl β-glucopyranoside, and named xylocoside A.

Compound **2**, an amorphous solid, had the same molecular formula $C_{17}H_{26}O_{10}$ as **1** on the basis of HR-ESI-MS. The ^{1}H- and ^{13}C-NMR (*Table 1*) showed that **2** is highly similar to **1**, except the chemical shift values of C(2) and C(1) shifted to δ(C) 83.0 and 63.7, compared to δ(C) 72.7 and 74.1, respectively, in **1**. An HMBC correlation from H–C(1″) (δ(H) 4.43) to C(2) (δ(C) 83.0) indicated that the glucose residue was connected to C(2). Thus, compound **2** was established as 1-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-yl β-glucopyranoside, and named xylocoside B.

Table 1. *NMR Data* (500 (^{1}H) and 125 MHz (^{13}C), CD_3OD) *for* **1**–**3** *and* **8**. δ in ppm, J in Hz.

Position	**1**		**2**		**3**		**8**
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	74.1	3.66 (*dd*, J = 10.5, 5.5), 3.57 (*dd*, J = 10.5, 4.0)	63.7	3.55 (*dd*, J = 12.0, 3.0), 3.40 (*dd*, J = 12.0, 6.0)	74.0	3.76 (*dd*, J = 10.0, 5.0), 3.52 (*dd*, J = 10.0, 4.0)	66.6
2	72.7	3.93–3.97 (*m*)	83.0	3.89–3.92 (*m*)	72.8	3.90–3.93 (*m*)	74.6
3	40.9	2.78 (*dd*, J = 14.0, 6.5), 2.69 (*dd*, J = 14.0, 7.0)	39.3	2.90 (*dd*, J = 13.5, 5.0), 2.73 (*dd*, J = 13.5, 8.5)	40.8	2.78 (*dd*, J = 13.5, 6.5), 2.68 (*dd*, J = 13.5, 7.0)	40.9
1′	130.5	–	130.1	–	130.4	–	130.8
2′	107.8	6.54 (*s*)	107.9	6.51 (*s*)	107.8	6.53 (*s*)	107.7
3′	149.1	–	149.0	–	149.1	–	149.1
4′	134.8	–	134.9	–	135.0	–	134.9
5′	149.1	–	149.0	–	149.1	–	149.1
6′	107.8	6.54 (*s*)	107.9	6.51 (*s*)	107.8	6.53 (*s*)	107.7
1″	104.6	4.27 (*d*, J = 8.0)	104.3	4.43 (*d*, J = 8.0)	104.8	4.26 (*d*, J = 8.0)	
2″	75.2	3.25 (*dd*, J = 9.0, 8.0)	75.5	3.19 (*dd*, J = 9.5, 8.0)	75.1	3.25 (*dd*, J = 9.0, 8.0)	
3″	78.0	3.37 (*t*, J = 9.0)	78.0	3.31 (*t*, J = 9.0)	77.7	3.37 (*t*, J = 9.0)	
4″	71.7	3.28–3.32 (*m*)	71.8	3.22–3.25 (*m*)	71.8	3.29–3.32 (*m*)	
5″	77.9	3.26–3.29 (*m*)	78.0	3.22–3.25 (*m*)	75.3	3.45–3.49 (*m*)	
6″	62.7	3.86 (*dd*, J = 10.5, 2.5), 3.82 (*dd*, J = 10.5, 5.5)	62.9	3.81 (*dd*, J = 12.0, 2.0), 3.61 (*dd*, J = 12.0, 5.5)	64.8	4.41 (*dd*, J = 12.0, 2.5), 4.19 (*dd*, J = 12.0, 6.0)	
1‴					54.0	2.64–2.66 (*m*)	
2‴					77.4	4.31 (ψ-*q*[a]), J = 6.5)	
3‴					35.6	1.83–1.90 (*m*), 1.53–1.59 (*m*)	
4‴					23.6	1.74–1.80 (*m*), 1.61–1.69 (*m*)	
5‴					29.0	1.96–2.03 (*m*), 1.70–1.76 (*m*)	
C=O					176.6	–	
MeO–C(3′,5′)	56.8	3.83 (*s*)	56.8	3.77 (*s*)	56.8	3.82 (*s*)	

[a]) ψ stands for *pseudo*.

HR-FAB-MS Data for compound **3** gave a quasimolecular ion peak $[M+H]^+$ at m/z 503.2121, suggesting the molecular formula $C_{23}H_{34}O_{12}$. The ^{1}H- and ^{13}C-NMR spectra of **3** (*Table 1*) showed similarity with those of **1**. Besides of the similar signals, additional signals of an ester CO group (δ(C) 176.6), one CH group (δ(C) 54.0), three CH_2 groups (δ(C) 35.6, 29.0, 23.6), and one CHO group (δ(C) 77.4) showed the presence of a (2-hydroxycyclopentyl)carbonyl moiety by comparison of the data with those in literature [18], which was supported by further ^{1}H,^{1}H-COSY and HMBC data (*Fig. 2*). The chemical shift of C(6″) at δ(C) 64.8 comparing with that of **1** at δ(C) 62.7, together with a HMBC correlation from CH_2(6″) (δ(H) 4.41, 4.19) to the CO group (δ(C) 176.6) indicated that the OH group at C(6″) position of the glucose was esterified by 2-hydroxycyclopentanecarboxylic acid. The *trans*-configuration of the (2-hydroxycyclopentyl)carbonyl fragment in positions 1‴ and 2‴ was determined by the large coupling constant of H–C(2‴) at δ(H) 4.31 (*ddd*, appearing as *pseudo-q*, J = 6.5), in comparison with the reported values for the *trans* (J = 6.5) and *cis* (J = 4.0)

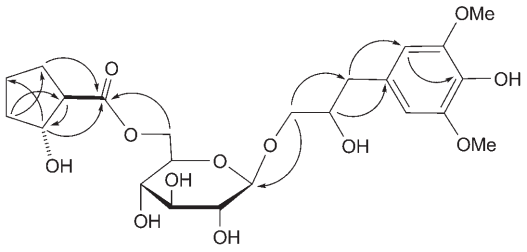

Fig. 2. *Selected HMBC of compound* **3**

configurations of 2-hydroxycyclopentanecarboxylic acid [18]. Furthermore, no correlation was found between H–C(1‴) and H–C(2‴) in the NOESY spectrum. The absolute configuration of **3** has not been determined. Consequently, compound **3** was elucidated as 2-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-1-yl 6-*O*-[(2-hydroxycyclopentyl)carbonyl]-*β*-D-glucopyranoside, and named xylocoside C.

Compound **4** was obtained as an amorphous solid. Its HR-FAB-MS spectrum exhibited an $[M+Na]^+$ ion at *m/z* 507.1838 (calc. 507.1842), compatible with the molecular formula $C_{23}H_{32}O_{11}$. By comparing its ^{1}H- and ^{13}C-NMR spectra (*Table 2*) with those of **3**, a *β*-{6′-*O*-[(2″-hydroxycyclopentyl)carbonyl]}glucosyl moiety (δ(H) 4.85, *d*, *J* = 8.0, H–C(1′)) was determined. The remaining NMR signals showed the presence of a 1,2,4,6-tetrasubstituted benzene ring, an (*E*)-alkene, a CH_2OH and two MeO groups, appearing as *singlet*s. Thus, compound **4** was determined to have the same aglycone as syringin [14]. An HMBC correlation from H–C(1′) to C(1) (δ(C) 135.5) indicated the glucose linked at C(1). Therefore, compound **4** was established to be 4-[(1*E*)-3-hydroxyprop-1-en-1-yl]-2,6-dimethoxyphenyl 6-*O*-[(2-hydroxycyclopentyl)-carbonyl]-*β*-D-glucopyranoside, and named xylocoside D.

Compound **5** was named xylocoside E. The HR-FAB-MS data gave the molecular formula $C_{21}H_{30}O_{11}$. The ^{1}H- and ^{13}C-NMR spectra showed high resemblance to those of **4**, exhibiting a *β*-{6′-*O*-[(2″-hydroxycyclopentyl)carbonyl]}glucosyl moiety, a tetrasubstituted aromatic ring, and two MeO and a CH_2OH groups. On the other hand, no olefinic C=C bond was observed. These different signals showed the aglycone of **5** to be a 2,6-dimethoxy-4-(hydroxymethyl)phenol moiety, the same aglycone as found in dimethylcrenatin [19]. A HMBC correlation from the anomeric H-atom (δ(H) 4.83, H–C(1′)) to C(1) (δ(C) 134.9) indicated that the glucose was connected to C(1). Consequently, compound **5** was confirmed as {6′-*O*-[(2″-hydroxycyclopentyl)carbonyl]}dimethylcrenatin ester.

The molecular formula of compound **6** was determined to be $C_{19}H_{26}O_{10}$ by the quasimolecular ion peak of $[M+Na]^+$ at *m/z* 437.1425 (calc. 437.1424) in HR-ESI-MS. Its ^{1}H- and ^{13}C-NMR data (*Table 2*) differed from **3**–**5** by the structure of the aglycone. The ^{1}H-NMR signals show a typical *ABX* coupling system (δ(H) 6.68 (*d*, *J* = 2.0), 6.64 (*d*, *J* = 7.5), 6.51 (*dd*, *J* = 7.5, 2.0)) and a MeO group, which were in agreement with the NMR data reported for tachioside [16]. Key HMBC data confirmed the aglycone to be 4-hydroxy-2-methoxyphenol, and the glucose residue connected at C(1). Thus, **6** was elucidated as *β*-{6′-*O*-[(2″-hydroxycyclopentyl)carbonyl]}tachioside ester, named as xylocoside F.

Table 2. *NMR Data* (500 (^{1}H) and 125 MHz (^{13}C), CD_3OD) *for* **4**–**6**. δ in ppm, J in Hz.

Position	**4**		**5**		**6**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
1	135.5	–	134.9	–	143.2	–
2	154.6	–	154.5	–	149.2	–
3	105.3	6.72 (*s*)	105.6	6.68 (*s*)	103.7	6.68 (*d*, *J* = 2.0)
4	135.3	–	139.7	–	152.5	–
5	105.3	6.72 (*s*)	105.6	6.68 (*s*)	110.1	6.51 (*dd*, *J* = 7.5, 2.0)
6	154.6	–	154.5	–	116.0	6.64 (*d*, *J* = 7.5)
7	131.3	6.54 (*dt*, *J* = 16.0, 1.5)	65.2	–	–	
8	130.0	6.32 (*dt*, *J* = 16.0, 5.5)	–	–	–	
9	63.6	4.21 (*dd*, *J* = 5.5, 1.5)	–	–	–	
1′	104.8	4.85 (*d*, *J* = 8.0)	104.9	4.83 (*d*, *J* = 8.0)	104.3	4.68 (*d*, *J* = 7.5)
2′	75.6	3.49 (*dd*, *J* = 9.0, 8.0)	75.6	3.48 (*t*, *J* = 8.0)	74.9	3.53 (*dd*, *J* = 9.0, 7.5)
3′	77.7	3.41 (*t*, *J* = 9.0)	77.8	3.41 (*t*, *J* = 8.0)	77.8	3.39 (*t*, *J* = 8.5)
4′	71.7	3.33–3.36 (*m*)	71.7	3.35–3.38 (*m*)	71.6	3.28–3.34 (*m*)
5′	75.6	3.36–3.38 (*m*)	75.6	3.35–3.38 (*m*)	75.4	3.30–3.36 (*m*)
6′	64.6	4.17 (*dd*, *J* = 11.5, 6.0), 3.35 (*dd*, *J* = 11.5, 2.0)	64.6	4.33 (*dd*, *J* = 11.5, 1.5), 4.17 (*dd*, *J* = 11.5, 5.5)	64.7	4.44 (*dd*, *J* = 12.0, 1.5), 4.14 (*dd*, *J* = 12.0, 6.5)
1″	54.1	2.55–2.59 (*m*)	54.1	2.56–2.60 (*m*)	54.1	2.60–2.64 (*m*)
2″	77.2	4.19 (ψ-*q*[a]), *J* = 6.5)	77.2	4.21 (ψ-*q*, *J* = 6.0)	77.2	4.29 (ψ-*q*, *J* = 6.0)
3″	35.5	1.77–1.83 (*m*), 1.48–1.54 (*m*)	35.5	1.78–1.83 (*m*), 1.52–1.60 (*m*)	35.5	1.82–1.86 (*m*), 1.51–1.56 (*m*)
4″	23.6	1.63–1.71 (*m*), 1.54–1.63 (*m*)	23.6	1.68–1.74 (*m*), 1.60–1.67 (*m*)	23.6	1.68–1.74 (*m*), 1.62–1.65 (*m*)
5″	28.9	1.84–1.91 (*m*), 1.54–1.63 (*m*)	28.9	1.88–1.93 (*m*), 1.60–1.67 (*m*)	29.1	1.94–1.97 (*m*), 1.68–1.74 (*m*)
C=O	176.3	–	176.3	–	176.4	–
MeO–C(2)	57.0	3.83 (*s*)	56.9	3.83 (*s*)	56.5	3.78 (*s*)
MeO–C(6)	57.0	3.83 (*s*)	56.9	3.83 (*s*)		

[a]) ψ stands for *pseudo*.

Compound **7** was isolated as a white amorphous solid. The HR-ESI-MS gave its molecular formula as $C_{17}H_{24}O_{11}$. In the ^{1}H-NMR spectrum (*Table 3*), a typical *ABCD* coupling system, a glucopyranosyl, and an arabinopyranosyl moiety were observed, suggesting the presence of an *ortho*-substituted benzene, and **7** to be a pyrocatechol-diglycoside [6]. The identity of the sugar residues was confirmed after acid hydrolysis by GC analysis of thiazolidine derivatives. Large coupling constants (J = 7.0) for the anomeric H-atom (δ(H) 4.69, *d*, H–C(1′)) of glucose suggesting the β-configuration, and the α-configuration for the arabinose was confirmed by the chemical shift of its anomeric C-atom in the ^{13}C-NMR data (δ(C) 104.9) [20]. The C(6′) signal appeared at δ(C) 69.5 suggested that the interglycosidic linkage was arabinosyl-(1″ → 6′)-glucose, which was further confirmed by HMBC experiment. An HMBC correlation from H–C(1′) (δ(H) 4.69) to C(1) (δ(C) 146.7) determined the glycosylation position. Therefore, compound **7** was identified as pyrocatechol-1-*O*-α-L-arabinopyranosyl-(1″ → 6′)-β-D-glucopyranoside, and named as xylocoside G.

In a recent study, we had reported the isolation of chaulmoogric acid from the same plant [2e]. This is an unusual cyclopentenoid fatty acid only found in some tribes of the

Table 3. *NMR Data* (500 (^{1}H) and 125 MHz (^{13}C), CD_3OD) *for* **7**. δ in ppm, J in Hz.

Position	δ(C)	δ(H)	HMBC
1	146.7 (*s*)	–	
2	148.4 (*s*)	–	
3	117.1 (*d*)	6.77 (*dd*, J = 8.0, 1.5)	C(1), C(2), C(4), C(5)
4	124.8 (*d*)	6.84 (*dt*, J = 8.0, 1.5)	C(2), C(3), C(5), C(6)
5	121.2 (*d*)	6.75 (*dt*, J = 8.0, 1.5)	C(1), C(3), C(4), C(6)
6	119.1 (*d*)	7.15 (*dd*, J = 8.0, 1.5)	C(1), C(2), C(4), C(5)
Glc			
1′	104.2 (*d*)	4.69 (*d*, J = 7.0)	C(1), C(3′), C(5′)
2′	74.8 (*d*)	3.40 – 3.42 (*m*)	C(1′)
3′	77.5 (*d*)	3.38 – 3.40 (*m*)	C(2′), C(4′)
4′	71.5 (*d*)	3.33 – 3.37 (*m*)	C(3′), C(5′)
5′	77.4 (*d*)	3.54 (*dt*, J = 6.5, 2.0)	C(1′)
6′	69.5 (*t*)	4.07 (*dd*, J = 11.5, 2.0), 3.71 (*dd*, J = 11.5, 6.5)	C(4′), C(1″)
Ara			
1″	104.9 (*d*)	4.26 (*d*, J = 7.0)	C(6′), C(3″), C(5″)
2″	72.5 (*d*)	3.57 (*dd*, J = 6.5, 2.5)	C(1″)
3″	74.1 (*d*)	3.45 (*dd*, J = 10.0, 4.0)	C(2″), C(4″)
4″	69.4 (*d*)	3.71 – 3.73 (*m*)	C(3″), C(5″)
5″	66.6 (*t*)	3.79 (*dd*, J = 11.5, 3.5), 3.43 (*dd*, J = 11.5, 2.0)	C(1″)

family Flacourtiaceae. Cyclopentenoid cyanohydrin glycosides, another group of interesting constituents, which were widely found in Flacourtiaceae and some closely related families, including Passifloraceae, Turneraceae, Malesherbiaceae, and Caricaceae. Both cyclopentenoid fatty acids and cyclopentenoid cyanohydrin glycosides owned the unique cyclopentenoid framework, which were proposed to be derived from the non-protein amino acid 2-cyclopentenyl-L-glycine. Efforts by *Spener et al.* towards the biosynthesis of this non-protein amino acid disclosed that the $C_5 + 2 \times C_1$ path was favored, although a $C_4 + C_3$ pathway can not be ruled out. Thus, the occurrence of these cyclopentenoid structures showed the evolution of a novel biosynthetic pathway and represented a unique taxonomic character [21]. Compounds **3**–**6** are a series of phenolic glycosides varied by the aglycones, among which the OH groups at C(6) of glucose are esterified by 2-hydroxycyclopentanecarboxylic acid. Considering the close relationship between these plants, the unique 2-hydroxycyclopentanecarboxylic acid fragment is possibly derived from the same non-protein amino acid. Interestingly, most of the cyclopentenoid compounds occurring from this biosynthetic pathway found in higher plants before had an unsaturated five-membered ring system. But in our study, the five-membered ring system is saturated and hydroxylated at the C(2) position, which had been rarely found in natural resources. Therefore, such a fragment can be considered as a useful chemotaxonomic marker of *X. controversum*.

Experimental Part

General. Column chromatography (CC): Silica gel (SiO_2; 200 – 300 mesh) (*Qingdao Marine Chemical Industrials Co. Ltd.*), *Sephadex LH-20* gel (*Pharmacia*), Octadecyl silica gel (*ODS*, 25 – 40 μm, *Merck*). For *ODS* CC, a N_2 pressure of 0.12 Mpa was applied. HPLC: *DIONEX P680* HPLC pump and

Sovlent Rock SOR-100, with a *Dionex Softron GmbH UVD 170U* detector; Column: *Waters' Prep Nova-Pak® HR C18* column, 6 μm 7.8 × 300 mm. GC: *Agilent 6890N* (*HP-5* capillary column (28 m × 0.32 mm, i.d.); detection, FID; detector temp. 260°; column temp. 180°; carrier gas, N_2; flow rate, 40 ml/min). Optical rotations: *Perkin-Elmer 243B* digital polarimeter. UV Spectra: *Shimadzu UV-2450* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *NEXUS-470 FTIR* (*Nicolet*) spectrometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR, HMQC, HMBC, ^{1}H,^{1}H-COSY, and NOESY Spectra: *Bruker-DRX-400* and *Varian-Inova-500* spectrometers; δ in ppm, *J* in Hz. ESI-MS: *QSTAR* mass spectrometer. HR-ESI-MS: *Bruker APEX IV FTMS* mass spectrometer. HR-FAB-MS: *Bruker APEX II* FT-ICR-MS spectrometer, in *m*/*z*, glycerol was used as matrix.

Plant Material. The stems of *Xylosma controversum* CLOS were collected in December 2004 from Fangchenggang City, Guangxi Province of China, and authenticated by Mr. *Chaoliang Zhang*, Medical Material Company of Guangxi Province. A voucher specimen (XY20041206) was deposited in the herbarium of Modern Research Centre for Traditional Chinese Medicine of Peking University.

Extraction and Isolation. The dried stems (62.6 kg) of *X. controversum* were finely pulverized and extracted with boiling 80% EtOH twice (2 × 400 l), each 3 h. After removal of the solvent under reduced pressure at 60°, the crude extract (650 g) was suspended in H_2O (2.1 l) and extracted with petroleum ether (PE; 3 × 2.0 l), AcOEt (3 × 2.0 l), and BuOH (3 × 2.0 l), successively, to give a PE fraction (158.9 g), an AcOEt fraction (52.2 g), and a BuOH fraction (236.9 g). The BuOH extract was subjected to CC (SiO_2; 1.5 kg; 9.5 × 10 cm; $CHCl_3$/MeOH 30:1, 10:1, 5:1, 1:1) to give 9 fractions (*Fr. 1–9*). *Fr. 1* (1.6 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 30:1) to yield 3,4,5-trimethoxyphenol [10] (52 mg) and catechol [7] (350 mg). *Fr. 2* (0.81 g) was subjected to CC (SiO_2; AcOEt/MeOH 60:1) to give *Fr. 2.1–2.2*. *Fr. 2.2* was separated on CC (*Sephadex LH-20*, $CHCl_3$/MeOH 1:1; then *ODS*, MeOH/H_2O 2:8) to yield pyrocatechol-1-*O*-*β*-apiofuranosyl-(1″ → 6′)-*β*-glucopyranoside [5] (300 mg). CC of *Fr. 4* (510 mg; SiO_2; AcOEt/MeOH 20:1) yielded *Fr. 4.1–4.3*. *Fr. 4.3* was subjected to CC (*Sephadex LH-20*, MeOH; then *ODS*, MeOH/H_2O 4:6) to afford *threo*-syringyl glycerol [12] (220 mg) and **4** (20 mg). *Fr. 5* (21.5 g) was subjected to CC (SiO_2; AcOEt/MeOH 40:1) to give *Fr. 5.1–5.6*. *Fr. 5.2* was applied to CC (*Sephadex LH-20*, $CHCl_3$/MeOH 1:1; then *ODS*, MeOH/H_2O 3:7) to yield **6** (104 mg). From *Fr. 5.3*, 3,4,5-trimethoxyphenol-1-*O*-*β*-glucopyranoside [10] (20 mg) was obtained. Purification of *Fr. 5.5* by CC (*ODS*, MeOH/H_2O 3:7) provided **5** (13 mg). *Fr. 5.4* was subjected to CC (SiO_2; $CHCl_3$/MeOH 1:1; then *Sephadex LH-20*, MeOH and $CHCl_3$/MeOH 1:1) to yield two subfractions (*A* and *B*), *Subfr. A* was resubjected to CC (*ODS*, MeOH/H_2O 3:7) to provide pyrocatechol-1-*O*-*β*-glucopyranoside [6] (3500 mg) and syringin [14] (320 mg), and *Subfr. B* was further separated by preparative TLC ($CHCl_3$/MeOH 4:1) to provide a mixture (15 mg) of *threo*-guaiacyl glycerol and *erythro*-guaiacyl glycerol [13]. *Fr. 5.6* was applied to CC (SiO_2; $CHCl_3$/MeOH 6:1) to obtain **3** (18 mg). *Fr. 6* (8.7 g) was subjected to CC (SiO_2; AcOEt/MeOH 20:1) to yield *Fr. 6.1–6.4*. *Fr. 6.2* was subjected to CC (*ODS*, MeOH/H_2O 2:8; then *Sephadex LH-20*, MeOH) to obtain tachioside (6 mg) and isotachioside (6 mg) [16]. *Fr. 6.3* was further separated by CC (SiO_2; AcOEt/MeOH 8:1, then *ODS*, MeOH/H_2O 2:8), yielding **8** (50 mg), 3,4,5-trimethoxyphenol-1-*O*-*β*-apiofuranosyl-(1″ → 6′)-*β*-glucopyranoside [8] (50 mg), and rhyncoside C [17] (45 mg). *Fr. 6.4* was subjected to CC (SiO_2; $CHCl_3$/MeOH 6:1) to give junipetroloside A [11] (102 mg), followed by reversed-phase *HPLC* (*RP-18*, MeOH/H_2O, 1.7:8.3) to yield **1** (6 mg) and **2** (20 mg). *Fr. 8* (9.8 g) was applied to CC (SiO_2; AcOEt/MeOH 10:1) to yield *Fr. 8.1–8.6*. *Fr. 8.2* was resubjected to CC (*Sephadex LH-20*, MeOH, then *ODS*, MeOH/H_2O 2:8) to yield 3,4,5-trimethoxyphenol (30 mg). Separation of *Fr. 8.5* by CC (SiO_2; $CHCl_3$/MeOH 3:1) yielded *Fr. 8.5.1–8.5.4*. Then, purification of *Fr. 8.5.2* by CC (*ODS*, MeOH/H_2O, 2.5:7.5) gave salirepin [15] (32 mg), and *Fr. 8.5.4* was separated by CC (*Sephadex LH-20*, MeOH; then *ODS*, MeOH/H_2O, 2.5:7.5) to give pyrocatechol-1-*O*-*β*-xylopyranosyl-(1″ → 6′)-*β*-glucopyranoside [6] (87 mg). Separation of *Fr. 8.6* by CC (SiO_2; $CHCl_3$/MeOH 3:1) led to *Fr. 8.6.1–8.6.4*. Purification of *Fr. 8.6.3* by CC (*ODS*, MeOH/H_2O, 2:8) yielded 3,4,5-trimethoxyphenol-1-*O*-*β*-xylopyranosyl-(1″ → 6′)-*β*-glucopyranoside [9] (20 mg), and of *Fr. 8.6.4* by CC (*ODS*, MeOH/H_2O, 3:7) gave **7** (104 mg).

Xylocoside A (=*2-Hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-1-yl β-Glucopyranoside*; **1**). Amorphous solid. $[\alpha]_D^{25} = -5.6$ ($c = 0.71$, MeOH). UV (MeOH): 273 (3.39), 208 (4.85). IR (KBr): 3414, 2926, 1612, 1518, 1463, 1430, 1330, 1220, 1115, 1078, 1033. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS: 413 ($[M+Na]^+$). HR-ESI-MS: 413.1425 ($[M+Na]^+$, $C_{17}H_{26}NaO_{10}^+$; calc. 413.1424).

Xylocoside B (=*1-Hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-yl β-Glucopyranoside*; **2**). Amorphous solid. $[\alpha]_D^{25} = -6.2$ ($c = 0.36$, MeOH). UV (MeOH): 272 (3.46), 211 (4.77). IR (KBr): 3385, 2932, 1613, 1519, 1463, 1430, 1330, 1221, 1116, 1077, 1029. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS: 413 ($[M + Na]^+$). HR-ESI-MS: 413.1426 ($[M + Na]^+$, $C_{17}H_{26}NaO_{10}^+$; calc. 413.1424).

Xylocoside C (=*2-Hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-1-yl 6-*O*-[(2-Hydroxycyclopentyl)carbonyl]-β-*D*-glucopyranoside*; **3**). Amorphous solid. $[\alpha]_D^{25} = +2.2$ ($c = 0.09$, MeOH). UV (MeOH): 275 (2.46), 207 (5.36). IR (KBr): 3406, 2941, 1726, 1614, 1519, 1461, 1429, 1391, 1361, 1333, 1243, 1197, 1164, 1114, 1078, 1044, 919, 820, 804. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS: 503 ($[M + H]^+$), 525 ($[M + Na]^+$). HR-FAB-MS: 503.2121 ($[M + H]^+$, $C_{23}H_{35}O_{12}^+$; calc. 503.2129).

Xylocoside D (=*6′-*O*-[(2″-Hydroxycyclopentyl)carbonyl]syringin Ester*; *4-[(1*E*)-3-Hydroxy-1-propen-1-yl]-2,6-dimethoxyphenyl 6-*O*-[(2-Hydroxycyclopentyl)carbonyl]-β-*D*-glucopyranoside*; **4**). Amorphous solid. $[\alpha]_D^{25} = +3.6$ ($c = 0.11$, MeOH). UV (MeOH): 266 (4.53), 222 (4.85). IR (KBr): 3461, 2946, 2892, 1706, 1588, 1509, 1459, 1419, 1399, 1339, 1241, 1207, 1125, 1083, 1062, 996, 962, 842, 823. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 507 ($[M + Na]^+$). HR-FAB-MS: 507.1838 ($[M + Na]^+$, $C_{23}H_{32}NaO_{11}^+$; calc. 507.1842).

Xylocoside E (=*6′-*O*-[(2″-Hydroxycyclopentyl)carbonyl]dimethylcrenatin Ester*; *4-(Hydroxymethyl)-2,6-dimethoxyphenyl 6-*O*-[(2-Hydroxycyclopentyl)carbonyl]-β-*D*-glucopyranoside*; **5**). Amorphous solid. $[\alpha]_D^{25} = +1.3$ ($c = 0.15$, MeOH). UV (MeOH): 207 (4.53). IR (KBr): 3458, 2959, 1703, 1597, 1508, 1460, 1424, 1401, 1332, 1247, 1213, 1125, 1079, 1063, 995, 959, 907, 810. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 481 ($[M + Na]^+$). HR-FAB-MS: 481.1683 ($[M + Na]^+$, $C_{21}H_{30}NaO_{11}^+$; calc. 481.1686).

Xylocoside F (=*6′-*O*-[(2″-Hydroxycyclopentyl)carbonyl]tachioside Ester*; *4-Hydroxy-2-methoxyphenyl 6-*O*-[(2-Hydroxycyclopentyl)carbonyl]-β-*D*-glucopyranoside*; **6**). Amorphous solid. $[\alpha]_D^{25} = +2.5$ ($c = 0.18$, MeOH). UV (MeOH): 285 (3.44), 224 (3.91), 203 (4.34). IR (KBr): 3393, 2920, 1719, 1616, 1513, 1453, 1370, 1276, 1199, 1073, 1031, 942, 844, 801. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 437 ($[M + Na]^+$). HR-ESI-MS: 437.1425 ($[M + Na]^+$, $C_{19}H_{26}NaO_{10}^+$; calc. 437.1424).

Xylocoside G (=*Pyrocatechol-1-*O*-α-*L*-arabinopyranosyl-(1″→6′)-β-*D*-glucopyranoside*; *2-Hydroxyphenyl 6-*O*-α-*L*-Arabinopyranosyl-β-*D*-glucopyranoside*; **7**). Amorphous solid. $[\alpha]_D^{25} = -48.7$ ($c = 0.27$, MeOH). UV (MeOH): 274 (3.38), 203 (4.02). IR (KBr): 3390, 2925, 1599, 1500, 1461, 1375, 1268, 1208, 1071, 1007, 948, 913, 853. ^{1}H- and ^{13}C- NMR: *Table 3*. ESI-MS: 427 ($[M + Na]^+$). HR-ESI-MS: 427.1223 ($[M + Na]^+$, $C_{17}H_{24}NaO_{11}^+$; calc. 427.1216).

Acid Hydrolysis and Sugar Analyses. A soln. of compound **7** (5 mg) in 10% HCl/dioxane 1:1 (5 ml) was heated at 80° for 4 h. After the dioxane was evaporated, the soln. was extracted with AcOEt (3 × 3 ml). The aq. layer was neutralized with $NaHCO_3$ and concentrated. The solid residue was dissolved in MeOH and analyzed by TLC ($CHCl_3$/MeOH/H_2O 8:5:1; detection by spraying with 95% EtOH/H_2SO_4/anisaldehyde 9:0.5:0.5 (*v*/*v*), followed by heating at 120° for 10 min): glucose (R_f 0.30) and arabinose (R_f 0.32).

The TLC results were confirmed by GC analyses. The MeOH soln. of the solid residue from the aq. layer was evaporated to dryness and dissolved in anh. pyridine (100 µl), and 0.1M L-cysteine methyl ester hydrochloride (200 µl) was added. The mixture was held at 60° for 1 h. Then, hexamethyldisilazane (HMDS)/chloro(trimethyl)silane/pyridine 2:1:10 (*Acros Organics*, Belgium) was added, and the mixture stirred at 60° for 30 min. The thiazolidine derivatives were analyzed by GC for sugar identification: D-glucose derivative (t_R 12.45 min) and L-arabinose derivative (t_R 3.18 min) [3c].

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