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水红木中两个新的酚苷成分*

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摘要：从水红木（*Viburnum cylindricum*）植物中分离出2个新化合物，1-phloroglucinyl-(6-methybutyryl)-β-D-glucopyranoside命名为cylindrin A（**1**），1-[4-(3-hydroxyl-propyl)]-pyrocatechol-(6-methybutyryl)-β-D-glucopyranoside，命名为cylindrin B（**2**），以及7个已知化合物tachioside（**3**），syingic acid-4-β-D-glucopyran oside（**4**），1-β-D-glucopyranosyloxy-3-methoxy-5-hydroxybenzene（**5**），4-hydroxy-3-methoxyphenol-1-O-β-D-glucoside（**6**），4-hydroxy-2，6-dimethoxyphenol-1-O-β-D-glucoside（**7**），phloroglucinol-1-O-β-D-glucoside（**8**），1-β-D-glucosyloxy-2-(3-methoxy-4-hydroxyphenyl) propane-1，3-diol（**9**）. 它们的结构经波谱方法得到鉴定。**3~9**为首次从该种植物中分离得到。

关键词：水红木；酚苷；cylindrin A；cylindrin B
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Two New Phenolic Glycosides from *Viburnum cylindricum* (Caprifoliaceae)

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Abstract: *Viburnum cylindricum* has been used in folk medicine in Yunnan. Two new phenolic glycosides, 1-phloroglucinyl-(6-methybutyryl)-β-D-glucopyranoside named cylindrin A (**1**), and 1-[4-3-hydroxyl-propyl)]-pyrocatechol-(6-methybutyryl)-β-D-glucopyranoside named cylindrin B (**2**), along with seven known phenolic glycosides tachioside (**3**), syingic acid-4-β-D-glucopyran oside (**4**), 1-β-D-glucopyranosyloxy-3-methoxy-5-hydroxybenzene (**5**), 4-hydroxy-3-methoxyphenol-1-O-β-D-glucoside (**6**), 4-hydroxy-2, 6-dimethoxyphenol-1-O-β-D-glucoside (**7**), phloroglucinol-1-O-β-D-glucoside (**8**), 1-β-D-glucosyloxy-2-(3-methoxy-4-hydroxyphenyl) propane-1, 3-diol (**9**) have been isolated from the EtOAc extracts of its aerial parts. Their structures were elucidated by means of spectroscopic method. Compounds **3-9** were isolated from this plant for the first time.

Key words: *Viburnum cylindricum*; Phenolic glycoside; cylindrin A; cylindrin B

Viburnum cylindricum Buch is widely distributed in tropical area of Asia, which has been used in folk medicine in Yunnan for the treatment of common cold, diarrhea, rheumatoid arthritis and tumefaction (Institutum Botanicum Kunmingense Academiae Sinicae, 1991). However, few chemical data are available on this plant. Several phytochemical investigations on other species of the genus *Viburnum* have shown that these species present diterpenoids (Miwa *et al*, 2001), irridoids (Nedyalka *et al*, 1988), triterpenoids (Yoshiyasu and Hiroyuki, 2002) and phenolic glycosides (Koichi *et al*, 1991). In our phytochemical investigation of the EtOAc-soluble fraction of an ethanol extracts of *V. cylindricum*, 1-phloroglucinyl-(6-methybutyryl)-β-D-glucopyranoside (**1**), 1-[4-(3-hydroxyl-propyl)]-pyrcoatechol-(6-methybutyryl)-β-D-glucopyranoside (**2**), were isolated along with seven known phenolic glycosides (**3-9**).

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Result and Discussion

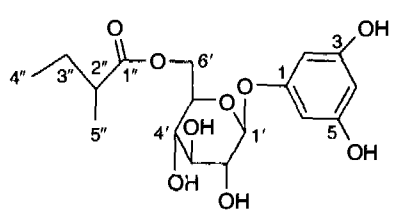
Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{25}$ −53 (*c* 0.4, MeOH). The molecular formula was assigned as $C_{17}H_{24}O_9$ from the HREIMS (*m/z* 371.1348, calcd. for *m/z* 371.1342, $C_{17}H_{24}O_9$ [M-H]$^-$) and the negative FABMS (*m/z* 371 [M-H]$^-$). The ^{13}C NMR spectrum showed signals of 17 carbons including two methyl groups and a carboxyl carbon. It exhibited signals belonging to a hexose moiety, a phloroglucinol and methylbutyryl moiety (Samlipto *et al*, 1988). They were approved by direct comparison with 1-[(2-methylbutyryl) phloroglucinyl]-β-D-glucopyranoside (A) (Samlipto *et al*, 1988). Both the ^{1}H and the ^{13}C NMR spectra data of **1** were similar to those of **8** (Yeap *et al*, 1989) except for methylbutyryl. Downfield carbons resonances (δ 160.7 and 2 × 160.1), attributed to three oxygenated carbons and three upfield methine carbon resonances (δ 98.1 and 2 × 96.9), were observed together with the hexose carbon resonances in the aliphatic region. Mythylbutyryl moiety was identified on the basis of HSQC and HMBC data (Table 2). The HSQC spectrum showed the connectivity between C-2″ (δ 42.2) and H-2″ (δ 2.44), C-3″ (δ 27.3) and H-3″ A (δ 1.64), H-3″ B (δ 1.45), C-4″ (δ 11.8) and H-4″ (δ 0.86), C-5″ (δ 16.8) and H-5″ (δ 1.13). The hexose moiety of compound **1** was identified as D-glucopyranosyl by means of its ^{1}H and ^{13}C NMR data (Tables 1 and 2) (Walker *et al*, 1976). The attachment of the phloroglucinol moiety at C-1′ and the attachment of the methylbutyryl group at C-6′ on the glucose was proved by HMBC experiments, according to a correlation between H-1′ (δ 4.82) and C-1′ (δ 160.7), H-6′ (δ 4.39, 4.13,) and C-1″ (δ 178.5). Compared with 1-[(2-methylbutyryl) phloroglucinyl]-β-D-glucopyranoside (Samlipto *et al*, 1988), **1** differs structurally in substituent position of methylbutyryl. Therefore, the structure of **1** is, 1-phloroglucinyl-(6-methylbutyryl)-β-D-glucopyranoside, named cylindrin A.

Table 1 ^{1}H-NMR assignment for compounds **1** (500 MHz) and **2** (400 MHz) (CD_3OD)

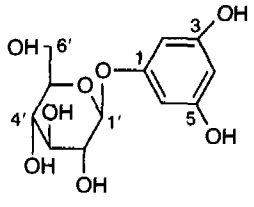
H	1		2	
	δ	H-H COSY	δ	H-H COSY
2	6.05 1H, d (*J* = 2.0)	4	6.95 1H, d (*J* = 1.7)	
3			6.95 1H, d (*J* = 1.7)	5
4	5.96 1H, t (*J* = 2.0)			
5			6.74 1H, dd (*J* = 1.7, 8.2)	3, 6
6	6.05 1H, d (*J* = 2.0)	4	6.72 1H, d (*J* = 8.2)	5
1′	4.82 1H, d (*J* = 6.8)	2′	4.71 1H, d (*J* = 6.8)	
2′	3.61 1H, m		3.60 1H, *m*	
3′	3.43 1H, m		3.51 1H, m	
4′	3.33 1H, m		3.35 1H, m	
5′	3.35 1H, m		3.44 1H, m	
6′A	4.41 1H, dd (*J* = 11.4, 2.0)		4.47 1H, dd (*J* = 11.9, 2.2)	
6′B	4.22 1H, dd (*J* = 11.4, 6.8)		4.17 1H, dd (*J* = 11.9, 6.4)	
2″	2.44 1H, m	5″, 3″A, 3″B	2.43 1H, m	5″, 3″A, 3″B
3″A	1.64 1H, m	2″, 3″B, 4″	1.63 1H, m	2″, 3″B, 4″
3″B	1.45 1H, m	2″, 3″A, 4″	1.46 1H, m	2″, 3″B, 4″
4″	0.86 3H, t (*J* = 7.4)	3″A, 3″B	0.85 3H, t (*J* = 7.6)	3″A, 3″B
5″	1.13 3H, d (*J* = 7.0)	2″	1.12 3H, d (*J* = 7.0)	2″
1‴			2.54 2H, t (*J* = 7.4)	2″
2‴			1.76 2H, m	1‴, 3‴
3‴			3.52 2H, t (*J* = 6.8)	2‴

Compound **2** was obtained as amorphous powder, with a molecular formula of $C_{20}H_{30}O_9$ indicated by the quasi-molecular ion peak at *m/z* 413 [M-H]$^-$ in its negative FABMS and *m/z* 413.1804 [M-H]$^-$ in its HREIMS (calcd. for $C_{20}H_{30}O_9$ *m/z* 413.1811), which also was supported by the ^{13}C NMR and DEPT spectral data. The spectral data were similar to those of **1**, except for three more methylene signal. Its phenolic cycle is 1, 2, 4-three substitute because ^{1}H NMR spectrum gave H-3 (δ 6.95, d, *J* = 1.7 Hz), H-5 (δ 6.74, dd, *J* = 1.7, 8.2 Hz) and H-6 (δ 6.72, d, *J* = 8.2 Hz). The attachment of the 3-hydroxyl-propyl moiety at C-4 was

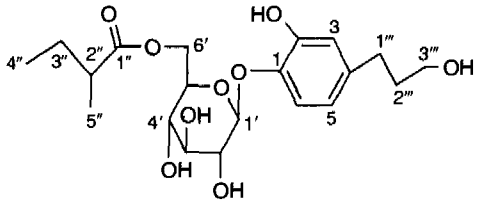
proved by HMBC experiments. There was a correlated cross-relaxation between the signal of H-1‴ (δ 2.54, t, J = 7.4) with that of C-4 (δ 135) and a correlation between H-3 (δ 6.95) with C-2 (δ 146.4) and C-4 (δ 135). There was also a correlation between H-5 (δ 6.74) and H-6 (δ 6.72) with C-1 (δ 146.5) (Table 2 and Fig. 2). The structure of **2** is, therefore, elucidated as 1-[4-(3-hydroxyl-propyl)]-pyrocatechol-(6-methybutyryl)- β - D - glucopyranoside, named cylindrin B.



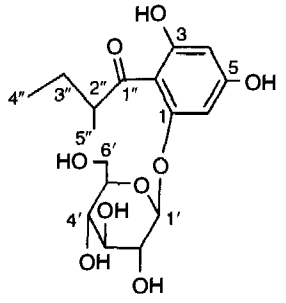
1



8



2



1-[[2-methylbutyryl] phloroglucinyl] -β-D-glucopyranoside

Fig. 1　Structures of compounds **1**, **2**, **8**

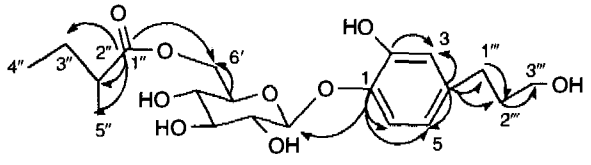


Fig. 2　Selected HMBC coorelations of **2**

Compounds **3 - 9** were characterized by comparing their spectral data ^{1}H, ^{13}C NMR, MS, IR and UV with those in the literature. Their structures (Fig. 1) were tachioside (**3**) (Shogo *et al*, 1987), syingic acid-4-β-D-glucopyranoside (**4**) (Kashiwada *et al*, 1986), 1-β-D-glucopyranosyloxy-3-methoxy-5-hydroxy benzene (**5**) (Koray *et al*, 1993), 4-hydroxy-3-methoxyphenol-1-O-β-D-glucoside (**6**) (Reiko *et al*, 1989), 4-hydroxy-2, 6-dimethoxyphenol-1-O-β-D-glucoside (**7**) (Shogo *et al*, 1987), phloroglucinol-1-O-β-D-glucoside (**8**) (Yeap *et al*, 1989), 1-β-D-glucosyloxy-2-(3-methoxy-4-hydroxyphenyl) propane-1, 3-diol (**9**) (Gilles *et al*, 1997).

Table 2　^{13}C-NMR assignment for compound **1** (125 MHz) and **2** (100 MHz) (CD_3OD)

C	**1** δ	Coupled to H HMBC	**2** δ	Coupled to H HMBC
1	160.7	2, 6, 1′	146.5	5, 6, 1′
2	96.9	4	146.4	3
3	160.1	2, 6	119.2	1‴
4	98.1	2, 6	135	3, 5, 1‴, 2‴
5	160.1	2, 6	124.8	6, 1‴
6	96.9	4	117	5
1′	101.9	2′	104.4	2′, 3′
2′	75.3	1′, 3′, 4′, 5′	75.6	1′, 3′, 4′, 5′
3′	77.9	2′, 4′, 5′	77.4	2′, 4′, 5′
4′	71.8	3′, 5′, 6′A, 6′B	71.6	3′, 5′, 6′A, 6′B
5′	74.8	4′, 6′A, 6′B	74.8	4′, 6′A, 6′B
6′	64.6	4′, 5′	64.6	4′, 5′
1″	178.5	6′A, 6′B, 2″, 3″A, 3″B, 5″	178.2	6′A, 6′B, 2″ 3″A, 3″B, 5″
2″	42.2	3″, 4″, 5″	42.3	3″, 4″, 5″
3″	27.3	2″, 4″, 5″	27.8	2″, 4″, 5″
4″	11.8	2″, 3″	11.9	2″, 3″
5″	16.8	2″, 3″	17	2″, 3″
1‴			32.4	2‴, 3‴
2‴			35.6	1‴, 3‴
3‴			62.2	1‴, 2‴

Experimental

General Experimental Procedures　Optical rotations were measured on a JASCO-20 polarimeter. UV spectra were recorded on a SHIMADZU 210A spectrophotometer. IR spectra were recorded on a Bio-Rad FTS-135 infrared spectrophotometer with KBr pellets. MS spectra were taken on a VG Auto Spce-3000. The 1D and 2D NMR experiments were performed on a BRUKER AM-400 or DRX-500 instruments. Column chromatography (CC) was performed with

silica gel (200-300 mesh, Qingdao Marine Chemical Inc., China), silica gel H (60 μm, Qingdao Marine Chemical Inc., China), Lichroprep RP_{18} gel (40-63 μm, Merck, Darmstadt, Germany), and Sephadex-LH-20 (25-100 μm, Amersham Biosciences, Sweden), TLC spots were detected by spraying with 5% H_2SO_4 in EtOH followed by heating.

Plant materials Dried stems and leaves of *V. cylindricum* were collected at Kunming, Yunnan, China in April 2004. The plant was identified by Dr. Li Rong. A voucher specimen (KUN No. 0085118) has been deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany Chinese academy of Sciences.

Extraction and Isolation Dried stems and leaves of *V. cylindricum* (11.2 kg) were extracted three times with 90% ethanol under reflux apparatus, and the extract was filtered. After evaporation of ethanol under reduced pressure, the concentrated extract was suspended in water and extracted with petroleum benzine, EtOAc, n-BuOH. The EtoAc extract (510 g) was subjected to column chromatography over silica gel (200-300 mesh), eluting with $CHCl_3$-MeOH (9:1-8:2) and divided into ten fractions.

Fraction 7 (40 g) as chromatographed on silica gel (200-300 mesh), developing with $CHCl_3$-MeOH (9:1-8:2) and divided into 14 subfractions (1-14). Subfractions 9-13 was rechromatographed on silica gel H, sephadexLH-20 (methanol and $CHCl_3$ 1:1), and purified by RP_{18} gel column chromatography using MeOH-H_2O (7:3) to yield compounds **1** (14 mg), **2** (16 mg), **3** (13 mg), **6** (11 mg).

Fraction 3 (3 g) were perform in same methods to yield compounds **7** (17 mg). Fraction 9 (60 g) was chromatographed on silica gel (200-300 mesh), developing with $CHCl_3$-MeOH (9:1-8:2) and divided into 16 subfractions (1-16). Subfractions 5-8 was rechromatographed on silica gel H, sephadexLH-20 (methanol and $CHCl_3$ 1:1), and purified by RP_{18} gel column chromatography using MeOH-H_2O (6:4) to yield compounds **4** (316 mg), **5** (24 mg), **8** (15 mg), **9** (12 mg).

Cylindrin A (1), $C_{17}H_{24}O_6$, amorphous powder; $[\alpha]_D^{25}$ -53 (*c* 0.4, MeOH). UV max (MeOH): 204, 275 nm; IR bands (KBr): 3421, 2925, 1714, 1610, 1462, 1159, 1074, 1010 cm^{-1}; Negative FAB-MS *m/z*: 371 [M-H]; HREIMS *m/z*: 371.1348 $[M-H]^-$; ^1H NMR (CD_3OD, 500 MHz) data see Table 1, ^{13}C NMR (CD_3OD, 125 MHz) data see Table 2.

Cylindrin B (2), amorphous powder; $[\alpha]_D^{25}$ -28.6 (*c* 0.3 MeOH); UV max (MeOH): 203, 280 nm; IR bands (KBr): 3429, 2934, 1719, 630, 1514, 1278, 1070 cm^{-1}; Negative FAB-MS *m/z*: 413 [M-H]; HREIMS *m/z*: 413.1804 $[M-H]^-$; ^1H NMR (CD_3OD, 400 MHz) data see Table1, ^{13}C NMR (CD_3OD, 100 MHz) data see Table 2.

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