

水红木中两个新的酚苷成分

朱向东, 汪琼, 王易芬, 鞠鹏, 罗士德

(中国科学院昆明植物研究所植物化学与西部植物资源可持续利用国家重点实验室, 云南昆明 650204)

摘要: 从水红木 (*Viburnum cylindricum*) 植物中分离出 2 个新化合物, 1-phlorogluciny-(6-methybutyryl)-D-glucopyranoside 命名为 cylindrin A (1), 1-[4-(3-hydroxyl-propyl)]-pyrocatechol-(6-methybutyryl)-D-glucopyranoside, 命名为 cylindrin B (2), 以及 7 个已知化合物 tachioside (3), syngic acid-4-D-glucopyranoside (4), 1-D-glucopyranosyloxy-3-methoxy-5-hydroxybenzene (5), 4-hydroxy-3-methoxyphenol-1-O-D-glucoside (6), 4-hydroxy-2, 6-dimethoxyphenol-1-O-D-glucoside (7), phloroglucinol-1-O-D-glucoside (8), 1-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

中图分类号: Q 946

文献标识码: A

文章编号: 0253-2700(2006)01-091-04

Two New Phenolic Glycosides from *Viburnum cylindricum* (Caprifoliaceae)

ZHU Xiang-Dong, WANG Qiong, WANG Yi-Fen, JU Peng, LUO Shi-De**

(State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China)

Abstract: *Viburnum cylindricum* has been used in folk medicine in Yunnan. Two new phenolic glycosides, 1-phlorogluciny-(6-methybutyryl)-D-glucopyranoside named cylindrin A (1), and 1-[4-(3-hydroxyl-propyl)]-pyrocatechol-(6-methybutyryl)-D-glucopyranoside named cylindrin B (2), along with seven known phenolic glycosides tachioside (3), syngic acid-4-D-glucopyranoside (4), 1-D-glucopyranosyloxy-3-methoxy-5-hydroxybenzene (5), 4-hydroxy-3-methoxyphenol-1-O-D-glucoside (6), 4-hydroxy-2, 6-dimethoxyphenol-1-O-D-glucoside (7), phloroglucinol-1-O-D-glucoside (8), 1-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-phlorogluciny-(6-methybutyryl)-D-glucopyranoside (1), 1-[4-(3-hydroxyl-propyl)]-pyrocatechol-(6-methybutyryl)-D-glucopyranoside (2), were isolated along with seven known phenolic glycosides (3-9).

基金项目: 国家高技术研究和发展计划 (863 计划) (2004AA2Z3321) 资助

通讯联系人 Corresponding author

收稿日期: 2005-06-29, 2005-08-10 接受发表

作者简介: 朱向东 (1965-) 男, 在读博士, 主要从事药用植物化学研究。

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 1H and the ^{13}C NMR spectra data of 1 were similar to those of 8 (Yeap *et al.*, 1989) except for methylbutyryl. Downfield carbon resonances (160.7 and 2×160.1), attributed to three oxygenated carbons and three upfield methine carbon resonances (98.1 and 2×96.9), were observed together with the hexose carbon resonances in the aliphatic region. Methyl-

butyryl moiety was identified on the basis of HSQC and HMBC data (Table 2). The HSQC spectrum showed the connectivity between C - 2 (42.2) and H - 2 (2.44), C - 3 (27.3) and H - 3 A (1.64), H - 3 B (1.45), C - 4 (11.8) and H - 4 (0.86), C - 5 (16.8) and H - 5 (1.13). The hexose moiety of compound 1 was identified as D-glucopyranosyl by means of its 1H 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 (4.82) and C - 1 (160.7), H - 6 (4.39, 4.13,) and C - 1 (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 1H -NMR assignment for compounds 1 (500 MHz) and 2 (400 MHz) (CD_3OD)

H	1		2	
		H-H COSY		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 1H NMR spectrum gave H - 3 (6.95, d, $J=1.7$ Hz), H - 5 (6.74, dd, $J=1.7, 8.2$ Hz) and H - 6 (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 (2.54, t, $J = 7.4$) with that of C - 4 (135) and a correlation between H - 3 (6.95) with C - 2 (146.4) and C - 4 (135). There was also a correlation between H - 5 (

6.74) and H - 6 (6.72) with C - 1 (146.5) (Table 2 and Fig. 2). The structure of 2 is, therefore, elucidated as 1-[4-(3-hydroxy-propyl)]-pyrocatechol-(6-methylbutyryl)- β -D-glucopyranoside, named cylindrin B.

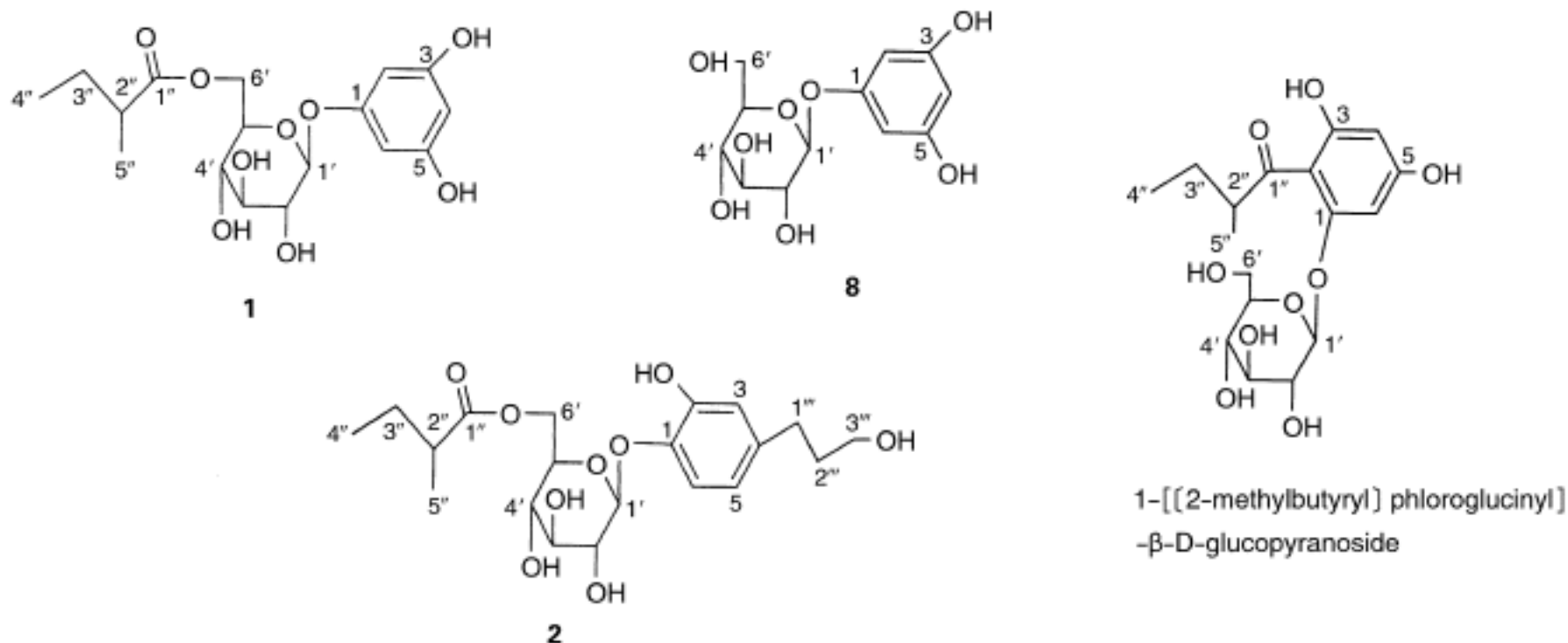


Fig. 1 Structures of compounds 1, 2, 8

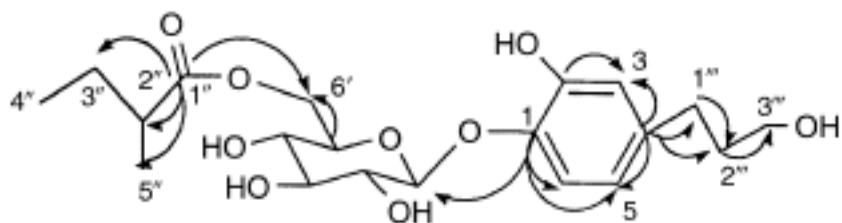


Fig. 2 Selected HMBC correlations of 2

Compounds 3 - 9 were characterized by comparing their spectral data ^1H , ^{13}C NMR, MS, IR and UV with those in the literature. Their structures (Fig. 1) were tachioside (3) (Shogo *et al*, 1987), syngic 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).

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

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

C	1	Coupled to H HMBC	2	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

on a Bio-Rad FTS-135 infrared spectrophotometer with KBr pellets. MS spectra were taken on a VG Auto Spec-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 RP₁₈ 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% H₂SO₄ 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 benzene, EtOAc, n-BuOH. The EtOAc extract (510 g) was subjected to column chromatography over silica gel (200 - 300 mesh), eluting with CHCl₃-MeOH (9:1-8:2) and divided into ten fractions.

Fraction 7 (40 g) as chromatographed on silica gel (200 - 300 mesh), developing with CHCl₃-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 CHCl₃ 1:1), and purified by RP₁₈ gel column chromatography using MeOH-H₂O (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 CHCl₃-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 CHCl₃ 1:1), and purified by RP₁₈ gel column chromatography using MeOH-H₂O (6:4) to yield compounds 4 (316 mg), 5 (24 mg), 8 (15 mg), 9 (12 mg).

Cylindrin A (1), C₁₇H₂₄O₉, 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 (CD₃OD, 500 MHz) data see

Table 1, ¹³C NMR (CD₃OD, 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 (CD₃OD, 400 MHz) data see Table 1, ¹³C NMR (CD₃OD, 100 MHz) data see Table 2.

References:

- Gilles C, Daovy PA, Albert JC, *et al*, 1997. Three phenylpropanoids from *Juniperus phoenicea* [J]. *Phytochemistry*, 44: 1169—1173
- Institutum Botanicum Kunmingense Academiae Sinicae, 1991. Flora Yunnanica Tomus . [M]. Beijing: Science Press
- Kashiwada Y, Nonaka G, Nishioka I, 1986. Tannins and related compounds. Isolation and characterization of new p-hydroxyphenyl butanones stilbenes and gallic glucosides [J]. *Chem Pharm Bull*, 34: 3237—3243
- Koichi M, Youko N, Masao K, 1991. Phenolic glycosides from *Viburnum dilatatu* [J]. *Phytochemistry*, 30: 2013—2014
- Koray M, Frank P, Adolf N, 1993. Two phioroglucinol glucosides, flavan gallates and flavonol glycosides from *Sedum sediforme* flowers [J]. *Phytochemistry*, 33: 171—174
- Miwa K, Ih-Sheng C, Yoshiyasu F, 2001. Vibsane-type diterpenes from Taiwannese *Viburnum odoratissimum* [J]. *Chem Pharm Bull*, 49: 242—245
- Nedyalka H, Iskra B, Bozhana M, *et al*, 1988. Two iridoids from *Viburnum lantana* [J]. *Phytochemistry*, 27: 3175—3179
- Reiko S, Gen-Ichiro N, Itsuo N, 1989. Phenol glucoside gallates from *Mallotus japonicus* [J]. *Phytochemistry*, 28: 2443—2446
- Samlipto K, Willem G, Van Der S, *et al*, 1989. Multifidol and multifidol glucoside from the latex of *Jatropha multifida* [J]. *Phytochemistry*, 28: 2439—2441
- Shogo I, Manami S, Hiroshi Ki O, *et al*, 1987. Aromatic glycosides from *Berchemia racemosa* [J]. *Phytochemistry*, 26: 2811—2814
- Walker TE, London RE, Whaley TW, *et al*, 1976. Carbon-13 nuclear magnetic resonance spectroscopy of [¹⁻¹³C] enriched monosaccharides [J]. *J Am Chem Soc*, 98: 5807—5813
- Yeap L, Foo L, Karchesy J, 1989. Polyphenolic glycosides from Douglas fir inner bark [J]. *Phytochemistry*, 28: 1237—1240
- Yoshiyasu F, Hiroyuki MF, 2002. Triterpenoids from *Viburnum suspensum* [J]. *Phytochemistry*, 60: 765—768