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岩芋中的一个新苯丙素苷*

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摘要: 从岩芋 (*Remusatia vivipara*) 干燥的球茎中分离得到 10 个化合物, 其中一个为新的苯丙素苷, 经波谱学分析及酸水解的方法确定该新化合物的结构为 Caffeyl alcohol-3-*O*-β-D-glucopyranoside。已知化合物包括 3 个苯丙素类 (松柏苷, caffeyl alcohol 和松柏醇), 3 个新木脂素 [4, 7, 9, 9'-tetrahydroxy-3, 3'-dimethoxy-8-*O*-4'-neolign-7'-ene, (7*R*, 8*S*)-^{7}-3, 3'-dimethoxy-4, 7, 9, 9'-tetrahydroxy-8-*O*-4'-neolignan-7-*O*-β-D-glucopyranoside, 以及 dehydrodiconiferyl alcohol-4-β-D-glucoside], 1 个酰胺 [(2*E*, 4*E*)-*N*-isobutyl-2, 4-decadienamide], 1 个甾体皂苷 (methyl proto-taccaoside) 和 1 个三萜皂苷 (saxifragifolin B)。所有化合物均为首次从岩芋属植物中分离得到。

关键词: 岩芋; 天南星科; 苯丙素苷
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A New Phenylpropanoid Glucoside from *Remusatia vivipara* (Araceae)

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Abstract: A new phenylpropanoid glucoside, caffeyl alcohol-3-*O*-β-D-glucopyranoside, together with nine known compounds, was isolated from the dry corms of *Remusatia vivipara* Schott. The structure of the new compound was determined by the spectroscopic method and acidic hydrolysis. The known compounds included three phenylpropanoids (coniferin, caffeyl alcohol and coniferyl alcohol), three neolignans [4, 7, 9, 9'-tetrahydroxy-3, 3'-dimethoxy-8-*O*-4'-neolign-7'-ene, (7*R*, 8*S*)-^{7}-3, 3'-dimethoxy-4, 7, 9, 9'-tetrahydroxy-8-*O*-4'-neolignan-7-*O*-β-D-glucopyranoside, and dehydrodiconiferyl alcohol-4-β-D-glucoside], an amide [(2*E*, 4*E*)-*N*-isobutyl-2, 4-decadienamide], a steroid saponin (methyl proto-taccaoside) and a triterpenoid saponin (saxifragifolin B). All compounds were isolated from the genus *Remusatia* for the first time.

Key words: *Remusatia vivipara*; Araceae; phenylpropanoid glucoside

Remusatia vivipara (Lodd.) Schott (Araceae) is a perennial herb mainly epiphytic on rocks and cliff-ledges in the subtropical forests of Asia such as SW China, Sri Lanka, Nepal, India, Myanmar, Thailand, Vietnam and Indonesia, and Cameroon in West Africa (Li, 1979). Its corms are strongly poisonous but used externally to treat breast mastitis, absces-

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ses, acariasis and so on (Health Bureau of Yunnan Province, 1973). Up to now, the chemical constituents of the plant have not been reported yet. So a phytochemical investigation of the *R. vivipara* was carried out, which led to the isolation of a new phenylpropanoid glucoside (1) from the corms, together with nine known compounds: coniferin (2) (Sugiyama *et al.*, 1993), caffeyl alcohol (3) (Quideau and Ralph, 1992), coniferyl alcohol (4) (Quideau and Ralph, 1992), 4, 7, 9, 9′-tetrahydroxy-3, 3′-dimethoxy-8-*O*-4′-neolign-7′-ene (5) (Lourith *et al.*, 2005), (7*R*, 8*S*) - $^{7'}$-3, 3′-dimethoxy-4, 7, 9, 9′-tetrahydroxy-8-*O*-4′-neolignan-7-*O*- -D-glucopyranoside (6) (Ma *et al.*, 2008), dehydrodiconiferyl alcohol-4- -D-glucoside (7) (Ye *et al.*, 2004), (2*E*, 4*E*) - *N*-isobutyl-2, 4-decadienamide (8) (Yasuda *et al.*, 1981), methyl proto-taccaoside (9) (Idaka *et al.*, 1991) and saxifragifolin B (10) (Waltho *et al.*, 1986). The structure elucidation of the new compound is reported.

Results and Discussion

Compound 1 was obtained as white amorphous powder. Negative HRESIMS analysis of the compound exhibited a quasimolcular ion peak at *m/z* 327.1083 [M-H]$^-$ (calcd, 327.1079), corresponding to the molecular formula $C_{15}H_{20}O_8$ for 1. Its IR spectrum showed absorption bands for hydroxy groups (3441 cm^{-1}) and a phenyl ring (1631 cm^{-1}, 1611 cm^{-1} and 1515 cm^{-1}). In the ^{13}C NMR spectrum of 1 (Table 1), 15 carbon signals including two oxygenated methylenes [δ_C 63.8 (C-9), 62.4 (C-6′)], ten methines [δ_C 131.5 (C-7), 127.5 (C-8), 123.4 (C-6), 117.0 (C-5), 116.5 (C-2), 104.4 (C-1′), 78.4 (C-5′), 77.6 (C-3′), 74.9 (C-2′), 71.4 (C-4′)] and three quaternary carbons [δ_C 148.1 (C-4), 146.9 (C-3), 130.8 (C-1)] were observed. The ^{1}H NMR spectrum of 1 (Table 1) displayed signals for an ABX benzene ring [δ_H 7.31 (1H, d, J = 1.6 Hz, H-2), 6.95 (1H, dd, J = 8.2, 1.6 Hz, H-6) and 6.77 (1H, d, J = 8.2 Hz, H-5)], a *trans*-allylic moiety [δ_H 6.48 (1H, d, J = 15.9 Hz, H-7), 6.20 (1H, dt, J = 15.9, 6.0 Hz, H-8) and 4.18 (2H, dd, J = 6.0, 1.1 Hz, H-9)]. In addition, its ^{1}H NMR spectrum showed an anomeric proton signal at δ 4.75 (1H, d, J = 7.1 Hz, H-1′), indicating the presence of a sugar moiety in 1. Acid hydrolysis of 1 yielded a D-glucose and determined by TLC and its optical rotation ($[\alpha]_D^{26.3}$ = 50.3 (*c* 0.055, H_2O)). The coupling constant (J = 7.1 Hz) of H-1′ and H-2′ deduced the glucose to be a -anomeric configuration.

Table 1 ^{1}H (500 MHz) and ^{13}C (100 MHz) NMR Data of 1 in CD_3OD (δ in ppm, J in Hz)

No.	δ_C	δ_H
1	130.8 (s)	
2	116.5 (d)	7.31 (d, J = 1.6)
3	146.9 (s)	
4	148.1 (s)	
5	117.0 (d)	6.77 (d, J = 8.2)
6	123.4 (d)	6.95 (dd, J = 8.2, 1.6)
7	131.5 (d)	6.48 (d, J = 15.9)
8	127.5 (d)	6.20 (dt, J = 15.9, 6.0)
9	63.8 (t)	4.18 (dd, J = 6.0, 1.1)
1′	104.4 (d)	4.75 (d, J = 7.1)
2′	74.9 (d)	3.49 (m)
3′	77.6 (d)	3.47 (m)
4′	71.4 (d)	3.39 (m)
5′	78.4 (d)	3.43 (m)
6′	62.4 (t)	3.91 (dd, J = 12.1, 2.2) 3.71 (dd, J = 12.1, 5.5)

In the HMBC spectrum (Fig. 1), H-7 showed correlations to C-2 and C-6, and H-8 showed to C-1, meanwhile H-2 and H-6 also showed correlations to C-1. These correlations indicated that the propenol moiety was placed at C-1. The assignments of C-3 and C-4 were ascertained by the HMBC correlation from H-5 to C-1 and C-3, H-6 to C-2 and C-4, H-2 to C-4 and C-6. The linkage of the -D-glucose substituent to C-3 was established by the correlation from H-1′ to C-3. Therefore, 1 was elucidated as caffeyl alcohol-3-*O*- -D-glucopyranoside.

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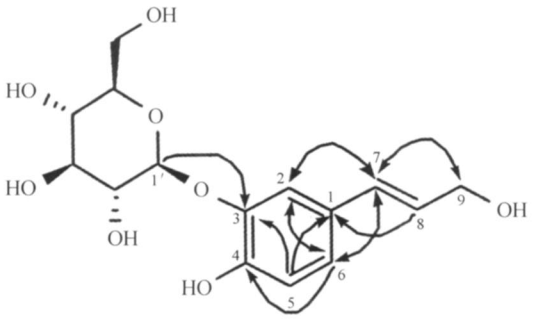

Fig. 1　Key HMBC correlations of 1

Experimental

General　MCI gel CHP 20P (75-150 μm, Mitsubishi Chemical Corporation, Tokyo), silica gel G (300-400 mesh, Qingdao Makall Group Co., Ltd), C_{18} silica gel (40-75 μm, Fuji Silysia Chemical Ltd.), silica gel H (10-40 μm), and Sephadex LH-20 (GE Healthcare Bio-Xciences AB) were used for column chromatography, and silica gel GF_{254} (Qingdao), for preparative TLC as pro-coated plates. The TLC spots were visualized under UV light and by dipping into 5% H_2SO_4 in alcohol, followed by heating. Semipreparative HPLC was carried out on an Agilent 1200 series pump equipped with a diode array detector and a Zorbax SB-C_{18} column (5.0 μm, 9.4 × 250 mm). 1D and 2D NMR spectra were obtained on BRUKER AM-400 and DRX-500 spectrometers with TMS as internal standard. MS analyses were performed on a VG Auto Spec-3000 mass spectrometer. Optical rotations were measured with a Horiba SEPA-300 polarimeter. UV spectra were determined on a Shimadzu double-beam210A spectrometer. IR spectra were measured on a Bio-Rad FTS-135 infrared spectrophotometer with KBr disks.

Plant material　The corms of *R. vivipara* were collected in October 2008 from Luxi City, Yunnan Province, People's Republic of China and identified by Dr. Hu Guang-Wan (Kunming Institute of Botany, Chinese Academy of Sciences). A voucher specimen (No. LX005) was deposited at the Laboratory of Ethnobotany, Kunming Institute of Botany.

Extraction and isolation　The air-dried, powdered corms of *R. vivipara* (1.0 kg) was exhaustively extracted with 95% EtOH (3 times) and then with MeOH (twice) under reflux. The crude extract (68 g) was suspended in H_2O and then partitioned successively with EtOAc and *n*-BuOH to obtain two fractions: EtOAc (A, 13 g), and *n*-BuOH (B, 6 g). Fr. B was subjected to column chromatography over MCI gel CHP 20P with MeOH-H_2O (a gradient elution of increasing concentration) and gained five fractions (B_1-B_5). Each fraction was further purified by repeated column chromatography (C_{18} silica gel, Sephadex LH-20, silica gel) and then semipreparative HPLC to obtain compounds. From Fr. B_1, compounds 1 (4.2 mg) and 2 (6.1 mg) were obtained. Fr. B_2 gave compound 6 (4.3 mg). Fr. B_4 afforded compounds 9 (30.7 mg) and 10 (15.2 mg). Fr. A was subjected to reversed-phase column chromatography over C_{18} silica gel eluting with a gradient of increasing MeOH in H_2O (5%-95%) and obtained five fractions (A_1-A_5). Subsequently, Fr. A_2 and A_4 were chromatographed on Sephadex LH-20 column, repeated silica gel column and then followed by semipreparative HPLC, to give compounds 3 (7.5 mg), 4 (4.6 mg), 5 (5.6 mg), and 7 (4.0 mg) from Fr. A_2 and 8 (3.5 mg) from Fr. A_4.

Acid hydrolysis of 1: A solution of 1 (4.0 mg) in 2 mol L^{-1} HCl (2 ml) was heated at 90 ℃ for 4 h. After evaporating the acidic solution, the reaction mixture was subjected to column chromatography over silica gel ($CHCl_3$-MeOH-H_2O, 3∶1∶0.05) to yield a D-glucose (1.1 mg), which was detected by TLC comparing with the authentic sample and its optical rotation, $[\alpha]_D^{26.3}$ 50.3 (*c* 0.055, H_2O).

Caffeyl alcohol-3-*O*-β-D-glucopyranoside (1): White amorphous powder; $[\alpha]_D^{25.5}$ 35.2 (*c* 0.125, MeOH); UV (MeOH) λ_{max}^{MeOH} (log ε) 263 (3.54) nm; IR ν_{max}^{KBr} cm^{-1}: 3441, 1631, 1610, 1515, 1283, 1074; ^1H and ^{13}C NMR (see Table 1); ESIMS *m/z* 363 $[M - Cl]^+$, 327 $[M - H]^-$; HRESIMS *m/z* 327.1083 $[M-H]^-$ (calcd for $C_{15}H_{19}O_8$, 327.1079).

Caffeyl alcohol (3): White amorphous powder (MeOH); ^1H NMR (CD_3OD, 400 MHz) δ: 6.86 (1H, *d*, *J* = 1.7 Hz, H-2), 6.68 (1H, *d*, *J* = 8.1 Hz, H-5), 6.71 (1H, *dd*, *J* = 8.1, 1.7 Hz, H-6), 6.42 (1H, *d*, *J* = 15.8 Hz, H-7), 6.10 (1H, *dt*, *J* = 15.8, 6.0 Hz, H-8), 4.16 (2H, *dd*, *J* = 6.0, 1.3 Hz, H-9); ESIMS *m/z* 165 $[M-H]^-$. This compound was determined according to its MS spectrum and by comparing its ^1H NMR data with compounds 1 and 4. Its ^1H NMR data were reported for the first time.

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