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# 珍珠荚蒾的化学成分研究

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**摘　要**:从珍珠荚蒾(*Viburnum foetidum* var. *ceanothoides*)的枝叶中分离得到14个化合物,经鉴定分别为:白桦醇(**1**),熊果醇(**2**),β-谷甾醇(**3**),白桦脂酸(**4**),熊果酸(**5**),对羟基苯甲酸(**6**),4,4′-二羟基-a-古柯间二酸(**7**),反式对香豆酸(**8**),顺式对香豆酸(**9**),红花菜豆酸(**10**),原儿茶酸(**11**),胡萝卜苷(**12**),1-*O*-(6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranosyl)-4-allylbenzene(**13**)和 apigenin 7-*O*-α-L-rhamnopyranosyl(1′′′→2′′)-β-D-glucopyranoside(**14**)。其中,化合物**1**、**7**、**9**、**10** 和 **13** 为首次从荚蒾属中分离得到;所有化合物均首次从珍珠荚蒾中分离得到。

**关键词**:珍珠荚蒾;化学成分
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# Chemical Constituents from the Stems and Leaves of *Viburnum foetidum* var. *ceanothoides*

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**Abstract**: Fourteen compounds were isolated from the stems and leaves of *Viburnum foetidum* var. *ceanothoides*. Their structures were identified as betulin (**1**), uvaol (**2**), β-sitosterol (**3**), betulinic acid (**4**), ursolic acid (**5**), p-hydroxybenzoic acid (**6**), 4,4′-dihydroxy-a-truxillic acid (**7**), E-p-coumaric acid (**8**), Z-p-coumaric acid (**9**), phaseic acid (**10**), protocatechuic acid (**11**), daucosterol (**12**), 1-*O*-(6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranosyl)-4-allylbenzene (**13**), and apigenin 7-*O*-α-L-rhamnopyranosyl(1′′′→2′′)-β-D-glucopyranoside (**14**). This is first report of the presence of compounds **1**, **7**, **9**, **10** and **13** in the genus *Viburnum* and **1-14** in this plant.

**Key words**: *Viburnum foetidum* var. *ceanothoides*; chemical constituents

## Introduction

*Viburnum foetidum* Wall. var. *ceanothoides* (C. H. Wright) Hand.-Mazz. belongs to the genus Viburnum (Adoxaceae), distributed in Yunnan, Sichuan and Guizhou provinces of China. The roots, stems, leaves and fruits have been used in Chinese folk medicines to treat stomatitis, eczema, fractures, bone-setters injury and trauma hemorrhage[1]. The phytochemical investigation on *V. foetidum* var. *ceanothoides* hasn't been reported so far. In our research, fourteen compounds were isolated. This is first report of the presence of compounds **1**, **7**, **9**, **10** and **13** in the genus *Viburnum* and **1-14** in this plant.

## Experimental

### General

The MS were measured on an Agilent 1100 series mass spectrometer or Waters UPLC Acquity/QTOFMS Premier. NMR spectra were measured on Bruker DRX-500 or Bruker Avance Ⅲ 400 instruments. Shimadzu LC-2010AHT HPLC System and Waters $C_{18}$ column (7.8 × 300 mm, 6 μm) were used for semipreparative HPLC. Silica gel for column chromatography and precoated silica $GF_{254}$ plates for TLC were produced by Qingdao Haiyang Chemical Co. Ltd. ODS and D101 macroporous resin were purchased from YMC Co. Ltd, Japan and Tianjin Haiguang Chemical Co. Ltd. respectively.

### Plant Material

The stems and leaves of *V. foetidum* Wall. var.

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*ceanothoides* were collected from Chengjiang County, Yunnan Province of China, in May 2008, and were identified by Associate Prof. Wang Meng-Yue. The voucher specimen of *V. foetidum* var. *ceanothoides* (No. 080530) was deposited at School of Pharmacy, Shanghai Jiao Tong University.

**Extraction and isolation**

The dried stems and leaves of *V. foetidum* var. *ceanothoides* (23 kg) were milled and extracted three times (3 × 2 L) with 75% EtOH for 2h each time, with the solvent removed under reduced pressure. The 75% ethanolic extract was suspended in water, and then was partitioned with petroleum ether, $CHCl_3$, EtOAc and n-BuOH successively. The petroleum ether-soluble fraction (90 g) was subjected to silica gel column eluting with a petroleum ether (PE)-EtOAc (100∶0 to 2∶1) gradient system to yield frs. 1-8. Fr. 4 was chromatographed on a silica gel column eluting with PE-$Me_2CO$ (8∶1) to provide frs. 4. 1-4. 5. Fr. 4. 2 followed by semipreparative HPLC (MeOH-$H_2O$;95∶5) to provide **1** (18.2 mg) and **2** (19.3 mg). The chloroform-soluble fraction (86 g) was subjected to silica gel column eluting with a PE-EtOAc (100∶0 to 1∶1) gradient system to yield frs. 1-10. After recrystallization of fr. 3 with $CH_3OH$, **3** (1.8 g) was obtained. Fr. 4 was chromatographed on a silica gel column eluting with PE-$Me_2CO$ (6∶1) to afford **4** (200 mg). Fr. 5 was chromatographed on a silica gel column eluting with PE-$Me_2CO$ (5∶1) to afford **5** (1.0 g). The EtOAc-soluble fraction (90 g) was subjected to silica gel column eluting with a $CH_2Cl_2$-$CH_3OH$ (100∶0 to 2∶1) gradient system to yield frs. 1-11. Fr. 3 was chromatographed on a silica gel column eluting with $CH_2Cl_2$-$CH_3OH$ (10∶1) to provide frs. 3. 1-3. 4. Fr. 3. 2 was further purified by semipreparative HPLC (MeCN∶$H_2O$ (containing 1‰ TFA) = 12∶88) to provide **6** (6.2 mg), **7** (10.6 mg), **8** (23.5 mg) and **9** (13.5 mg). Fr. 4 was purified by preparative TLC with $CHCl_3$-$CH_3OH$-HCOOH (100∶25∶1), **10** (24.2 mg) and **11** (50.3 mg) were obtained. Fr. 6 was applied to silica gel and eluted with $CH_2Cl_2$-$CH_3OH$ (10∶1) to afford **12** (2.0 g). The n-BuOH-soluble fraction (320 g) was subjected to a macroporous resin column with a gradient elution (20%, 40%, 60%, 80%, 95% EtOH/$H_2O$) to yield frs. 1-5. Fr. 2 and Fr. 3 was chromatographed on a silica gel column eluting with $CH_2Cl_2$-$CH_3OH$ (50∶1 to 2∶1) to yield frs. 2. 1-2. 8. Fr. 2. 3 was subjected to an ODS column eluting with 30% MeOH/$H_2O$ to afford Fr. 2. 3. 1-2. 3. 5. Fr. 2. 3. 3 was purified by preparative TLC with $CHCl_3$-$CH_3OH$-$H_2O$-HCOOH (60∶40∶10∶1) to provide **13** (58.2 mg). Fr. 2. 5 was subjected on silica gel column eluting with $CH_2Cl_2$-$CH_3OH$ (5∶1) to afford **14** (1.2 g).

## Identification

**Betulin** (**1**) $C_{30}H_{50}O_2$, white powder, ESI-MS *m/z*: 465.2 [M + Na]$^+$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$: 3.19 (1H, dd, $J$ = 11.5, 4.5 Hz, H-3$\alpha$), 2.38 (1H, m, H-19), 3.34 (1H, d, $J$ = 11.0 Hz, H-28$\alpha$), 3.80 (1H, dd, $J$ = 11.0, 1.5 Hz, H-28$\beta$), 4.58 (1H, brs, H-29$\alpha$), 4.68 (1H, brs, H-29$\beta$), 0.97, 0.76, 0.83, 1.02, 0.98, 1.68 (each 3H, s, 6 × $CH_3$, H-23, 24, 25, 26, 27, 30); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$: 38.6 (C-1), 27.3 (C-2), 79.0 (C-3), 38.8 (C-4), 55.2 (C-5), 18.3 (C-6), 34.2 (C-7), 40.9 (C-8), 50.3 (C-9), 37.1 (C-10), 20.8 (C-11), 25.1 (C-12), 37.2 (C-13), 42.7 (C-14), 27.0 (C-15), 29.1 (C-16), 47.7 (C-17), 48.7 (C-18), 47.7 (C-19), 150.5 (C-20), 29.7 (C-21), 33.9 (C-22), 28.0 (C-23), 15.4 (C-24), 16.1 (C-25), 15.9 (C-26), 14.7 (C-27), 60.5 (C-28), 109.7 (C-29), 19.1 (C-30). The NMR spectral data were in consistent with those reported [2].

**Uvaol** (**2**) $C_{30}H_{50}O_2$, white powder, ESI-MS *m/z*: 465.3 [M + Na]$^+$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$: 5.14 (1H, t, $J$ = 3.2 Hz, H-12), 3.53 (1H, d, $J$ = 8.8 Hz, H-28), 3.21 (2H, m), 1.11, 1.00, 0.99, 0.95, 0.80 (each 3H, s, 5 × $CH_3$), 0.94 (3H, d, $J$ = 7.2 Hz, H-30), 0.81 (3H, d, $J$ = 5.0 Hz, H-29); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$: 38.7 (C-1), 27.2 (C-2), 79.0 (C-3), 38.8 (C-4), 55.1 (C-5), 18.3 (C-6), 35.2 (C-7), 39.4 (C-8), 47.6 (C-9), 38.0 (C-10), 26.0 (C-11), 125.0 (C-12), 138.7 (C-13), 42.0 (C-14), 29.7 (C-15), 23.4 (C-16), 36.9 (C-17), 54.0 (C-18), 39.3 (C-19), 40.0 (C-20), 32.8 (C-21), 30.6 (C-22), 28.7 (C-23), 15.6 (C-24), 15.7 (C-25), 17.4 (C-26), 23.3 (C-27), 70.0 (C-28), 16.8 (C-29),

21.3(C-30). The NMR spectral data were in consistent with those reported [3].

**Betulinic acid (4)** $C_{30}H_{48}O_3$, white powder, ESI-MS *m/z*:455.3[M - H]$^-$; $^1$H NMR($C_5D_5N$,400 MHz) $\delta$:1.82(1H,m,H-2),3.42(1H,t,*J*=7.2 Hz,H-3), 2.71(1H, m, H-13), 1.51(1H, m, H-16$\alpha$), 2.62 (1H,d,*J*=11.7 Hz,H-16$\beta$),3.51(1H,m,H-19), 4.92(1H, s, H-29$\alpha$), 4.74(1H, s, H-29$\beta$), 0.78, 0.98, 1.02, 1.03, 1.19, 1.76 (each 3H, s, 6 × $CH_3$); $^{13}$C NMR($C_5D_5N$,100 MHz) $\delta$:40.5(C-1), 29.6(C-2), 79.3(C-3), 40.8(C-4), 57.2(C-5), 20.0(C-6), 36.1(C-7), 42.3(C-8), 52.2(C-9), 38.8(C-10), 22.4(C-11), 27.4(C-12), 39.8(C-13), 44.1(C-14), 31.5(C-15), 34.1(C-16), 57.9 (C-17), 51.0(C-18), 49.0(C-19), 152.6(C-20), 32.5(C-21), 38.9(C-22), 29.9(C-23), 17.6(C-24), 17.7(C-25), 17.7(C-26), 16.1(C-27), 180.1 (C-28), 111.2(C-29), 20.7(C-30). The NMR spectral data were in consistent with those reported [4].

***p*-Hydroxybenzoic acid (6)** $C_7H_6O_3$, white powder, HR-TOF MS *m/z*:139.0395[M + H]$^+$, 137.0239 [M - H]$^-$; $^1$H NMR(DMSO-$d_6$,500 MHz) $\delta$:6.80 (2H,d,*J*=8.0 Hz,H-3,5), 7.78(2H,d,*J*=8.0 Hz, H-2,6), 10.27(1H,s,OH), 12.40(1H,s,COOH). The NMR spectral data were in consistent with those reported [5].

**4,4′-Dihydroxy-a-truxillic acid (7)** $C_{18}H_{16}O_6$, white powder, HR-TOF-MS *m/z*: 327.0847 [M - H]$^-$; $^1$H NMR(DMSO-$d_6$,500 MHz) $\delta$:3.65(2H,m, H-$\beta$,$\beta'$), 4.12(2H,m,H-$\alpha$,$\alpha'$), 6.69(4H,d,*J*=8.5 Hz,H-3,3′,5,5′), 7.11(4H,d,*J*=8.5 Hz,H-2,2′, 6,6′), 9.30(2H, s, 2 × OH), 11.98(2H, s, 2 × COOH); $^{13}$C NMR(DMSO-$d_6$,125 MHz) $\delta$:40.3(C-$\alpha$,$\alpha'$), 46.7(C-$\beta$,$\beta'$), 114.9(C-3,3′,5,5′), 128.6 (C-2,2′,6,6′), 129.6(C-1,1′), 156.1(C-4,4′), 173.1(2 × COOH). The $^1$H NMR spectral data were in consistent with those reported [6].

**E-p-Coumaric acid (8)** $C_9H_8O_3$, white powder, HR-TOF-MS *m/z*:165.0552[M + H]$^+$, 163.0397[M - H]$^-$。$^1$H NMR($CD_3OD$,500 MHz) $\delta$:7.60(1H,d, *J*=16.0 Hz,H-7), 7.44(2H,d,*J*=8.5 Hz,H-2,6), 6.80(2H,d,*J*=8.5 Hz,H-3,5), 6.28(1H,d,*J*= 16.0 Hz,H-8). The NMR spectral data were in consistent with those reported [7].

**Z-p-Coumaric acid (9)** $C_9H_8O_3$, white powder, HR-TOF MS *m/z*:165.0551[M + H]$^+$, 163.0397[M - H]$^-$; $^1$H NMR($CD_3OD$,500 MHz) $\delta$:7.61(2H,d, *J*=8.5 Hz,H-2,6), 6.78(1H,d,*J*=12.5 Hz,H-7), 6.74(2H,d,*J*=8.5 Hz,H-3,5), 5.78(1H,d,*J*= 12.5 Hz,H-8). The NMR spectral data were in consistent with those reported [7].

**Phaseic acid (10)** $C_{15}H_{20}O_5$, white powder, APCI-MS *m/z*:279.1[M - H]$^-$; $^1$H NMR($CD_3OD$,500 MHz) $\delta$:1.01(3H,s,H-9′), 1.21(3H,s,H-7′), 2.07 (3H,d,*J*=1.0 Hz,H-6), 2.38(1H,dd,*J*=18.0,2.5 Hz,H-5′pro-R), 2.47(1H,dd,*J*=17.5,2.5 Hz,H-3′ pro-S), 2.70(1H,dd,*J*=18.0,2.5 Hz,H-5′pro-S), 2.80(1H,d,*J*=18.0 Hz,H-3′pro-R), 3.66(1H,d,*J* =8.0 Hz, H-8′pro-S), 3.94(1H,dd,*J*=8.0,2.5 Hz,H-8′pro-R), 5.79(1H,brs,H-2), 6.45(1H,d,*J* =15.5 Hz,H-5), 8.10(1H,d,*J*=15.5 Hz,H-4); $^{13}$C NMR($CD_3OD$,125 MHz) $\delta$:170.0(C-1), 120.2 (C-2), 151.4(C-3), 133.2(C-4), 133.9(C-5), 21.5 (C-6), 83.2(C-1′), 88.1(C-2′), 54.3(C-3′), 211.2 (C-4′), 53.5(C-5′), 49.8(C-6′), 19.7(C-7′), 78.9 (C-8′), 16.1(C-9′). The NMR spectral data were in consistent with those reported [8].

**Protocatechuic acid (11)** $C_7H_6O_4$, white powder, APCI-MS *m/z*:152.9[M - H]$^-$; $^1$H NMR($CD_3OD$, 500 MHz) $\delta$:6.73(1H,d,*J*=8.5 Hz,H-5), 7.35 (1H,dd,*J*=8.5,2.0 Hz,H-6), 7.42(1H,d,*J*=2.0 Hz,H-2). The NMR spectral data were in consistent with those reported [9].

**1-*O*-(6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranosyl)-4-allylbenzene(13)** $C_{21}H_{30}O_{10}$, white powder, ESI-MS *m/z*:465.2[M + Na]$^+$; $^1$H NMR($CD_3OD$, 500 MHz) $\delta$:1.22(3H,d,*J*=6.0 Hz,H-6″), 3.33 (3H,m,H-3′,H-4,H-4″), 3.38(2H,m,H-7), 3.47 (1H,m,H-2′), 3.55(1H,m,H-5′), 3.62(1H,dd,*J* =11.0,6.5 Hz,H-6′α), 3.68(1H,dd,*J*=6.0,3.0 Hz,H-5″), 3.72(1H,dd,*J*=9.5,3.5 Hz,H-3″), 3.86(1H,m,H-2″), 4.03(1H,dd,*J*=11.0,1.5 Hz, H-6′$\beta$), 4.73(1H,d,*J*=1.0 Hz,H-1″), 4.82(1H, d,H-1′), 5.02(1H,m,H-9α), 5.06(1H,m,H-9$\beta$), 5.94(1H,m,H-8), 7.03(2H,d,*J*=8.5 Hz,H-3,5), 7.12(2H,d,*J*=8.5 Hz,H-2,6); $^{13}$C NMR($CD_3OD$,

125 MHz) $\delta$: 157.4 (C-1), 117.9 (C-2), 130.5 (C-3), 135.3 (C-4), 130.5 (C-5), 40.3 (C-7), 139.1 (C-8), 115.7 (C-9), 102.5 (C-1′), 74.9 (C-2′), 78.0 (C-3′), 71.5 (C-4′), 76.8 (C-5′), 67.8 (C-6′), 102.1 (C-1″), 72.4 (C-2″), 72.1 (C-3″), 74.0 (C-4″), 69.8 (C-5″), 17.9 (C-6″). The NMR spectral data were in consistent with those reported [10].

**Apigenin 7-*O*-$\alpha$-*L*-rhamnopyranosyl (1‴→2″)-$\beta$-D-glucopyranoside (14)** $C_{27}H_{30}O_{14}$, yellow needles, ESI-MS *m/z*: 579.2 $[M+H]^+$; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 1.20 (3H, d, $J$ = 6.0 Hz, H-6‴), 5.13 (brs, H-1‴), 5.23 (1H, d, $J$ = 7.5 Hz, H-1″), 6.37 (1H, d, $J$ = 2.0 Hz, H-6), 6.79 (1H, d, $J$ = 2.0 Hz, H-8), 6.88 (1H, s, H-3), 6.95 (2H, d, $J$ = 9.0 Hz, H-3′, 5′), 7.94 (2H, d, $J$ = 8.5 Hz, H-2′, 6′); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 164.2 (C-2), 103.2 (C-3), 182.0 (C-4), 161.4 (C-5), 99.3 (C-6), 162.5 (C-7), 94.5 (C-8), 157.0 (C-9), 105.4 (C-10), 121.0 (C-1′), 128.5 (C-2′, 6′), 116.0 (C-3′, 5′), 161.1 (C-4′), 97.8 (C-1″), 76.2 (C-2″), 77.2 (C-3″), 69.6 (C-4″), 77.0 (C-5″), 60.4 (C-6″), 100.4 (C-1‴), 70.5 (C-2‴), 70.4 (C-3‴), 71.8 (C-4‴), 68.3 (C-5‴), 18.0 (C-6‴). The NMR spectral data were in consistent with those reported [11].

$\beta$-Sitosterol (**3**), ursolic acid (**5**) and daucosterol (**12**) were identified by comparison of $R_f$ value with the authentic samples.

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