小叶山葡萄的化学成分研究

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摘　要：目的　研究中国台湾传统中药材小叶山葡萄 *Vitis thunbergii* var. *taiwaniana* 的化学成分。**方法**　利用大孔树脂、Sephadex LH-20、ODS 及正相硅胶柱等色谱手段进行分离，通过多种波谱学数据分析进行单体化合物的结构鉴定。**结果**　从小叶山葡萄 60%乙醇提取物中分离得到 12 个化合物，分别鉴定为白藜芦醇（**1**）、*trans*-ε-viniferin（**2**）、(7*R*, 8*R*)-*threo*-4, 7, 9, 9′-tetrahydroxy-3, 3′-dimethoxy-8-*O*-4′-neolignan 7-*O*-β-*D*-glucopyranoside（**3**）、(7*S*, 8*R*)-urolignoside（**4**）、schizandriside（**5**）、vitisin A（**6**）、vitisin B（**7**）、davidiol A（**8**）、3, 5, 4′-trihydroxystilbene 4′-*O*-β-*D*-glucopyranoside（**9**）、蛇葡萄素 C（**10**）、(7*R*, 8*S*)-dihydrodehydrodiconiferyl alcohol 9-*O*-β-*D*-glucopyranoside（**11**）、表儿茶素（**12**）。**结论**　化合物 **3**～**5** 为首次从葡萄属中分离，化合物 **8**、**9**、**11**、**12** 为首次从小叶山葡萄中分离。

关键词：小叶山葡萄；葡萄属；白藜芦醇；蛇葡萄素 C；表儿茶素

中图分类号：R284.1　　**文献标志码：**A　　**文章编号：**0253 - 2670(2013)06 - 0660 - 05

DOI: 10.7501/j.issn.0253-2670.2013.06.005

Chemical constituents of *Vitis thunbergii* var. *taiwaniana*

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Abstract: Objective　To study the chemical constituents in *Vitis thunbergii* var. *taiwaniana* specially grown in Taiwan, China. **Methods**　The compounds were isolated by repeated HP20 macroporous adsorption resin column combined with Sephadex LH-20, ODS, and silica gel column chromatography. Their structures were identified on the basis of extensive spectroscopic data analysis and by comparison of their spectral data reported. **Results**　Twelve compounds were identified as resveratrol (**1**), *trans*-ε-viniferin (**2**), (7*R*, 8*R*)-*threo*-4, 7, 9, 9′-tetrahydroxy-3, 3′-dimethoxy-8-*O*-4′-neolignan 7-*O*-β-*D*-glucopyranoside (**3**), (7*S*, 8*R*)-urolignoside (**4**), schizandriside (**5**), vitisin A (**6**), vitisin B (**7**), davidiol A (**8**), 3, 5, 4′-trihydroxystilbene 4′-*O*-β-*D*-glucopyranoside (**9**), ampelopsin C (**10**), (7*R*, 8*S*)-dihydrodehydrodiconiferyl alcohol 9-*O*-β-*D*-glucopyranoside (**11**), and epicatechin (**12**). **Conclusion**　Compounds **3**—**5** are separated from the plants of *Vitis* L. for the first time, and compounds **8**, **9**, **11**, and **12** are separated from *V. thunbergii* var. *taiwaniana* for the first time.

Key words: *Vitis thunbergii* var. *taiwaniana* Lu; *Vitis* L.; resveratrol; ampelopsin C; epicatechin

小叶山葡萄 *Vitis thunbergii* var. *taiwaniana* Lu 属于葡萄科（Vitaceae）葡萄属 *Vitis* L. 植物，主要分布于中国台湾地区，以及日本、韩国等国家，多见于平地及山麓丛林内，中高地带也可偶尔见到。作为台湾传统中药，小叶山葡萄具有抑菌[1]、抗炎[2]、神经保护[3]等功效。然而，目前国内外对其化学成分研究并不系统，分离到的化合物主要以芪类化合物为主[2-3]。本研究利用多种分离分析手段，对小叶山葡萄地上部分的化学成分进行研究，从中分离得到 12 个化合物，分别鉴定为白藜芦醇（**1**）、*trans*-ε-

收稿日期：2012-10-02

基金项目：厦门市重大科技计划项目（3502Z20100006）

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viniferin（**2**）、(7*R*, 8*R*)-*threo*-4, 7, 9, 9′-tetrahydroxy-3, 3′-dimethoxy-8-*O*-4′-neolignan 7-*O*-β-*D*-glucopyranoside（**3**）、(7*S*, 8*R*)-urolignoside（**4**）、schizandriside（**5**）、vitisin A（**6**）、vitisin B（**7**）、davidiol A（**8**）、3, 5, 4′-trihydroxystilbene 4′-*O*-β-*D*-glucopyranoside（**9**）、蛇葡萄素 C（**10**）、(7*R*, 8*S*)-dihydrodehydrodiconiferyl alcohol 9-*O*-β-*D*-glucopyranoside（**11**）、表儿茶素（**12**）。其中，化合物 **3**～**5** 为首次从葡萄属中分离，化合物 **8**、**9**、**11**、**12** 为首次从小叶山葡萄中分离。

1 仪器与试剂

Bruker Avance II 400 型核磁共振仪（瑞士布鲁克公司）。3200 Q-trap 质谱仪（美国 ABI 公司）。各种色谱硅胶均系青岛海洋化工厂生产，HP20 大孔树脂为三菱化学株式会社生产，ODS、Sephadex LH-20 为 Pharmacia 公司进口分装产品，岛津 LC—20AD 高效液相色谱仪。

小叶山葡萄干粉由台湾台中荣民总医院教学研究部提供，由台中荣民总医院徐士兰教授鉴定为小叶山葡萄 *Vitis thunbergii* var. *taiwaniana* Lu，标本（XYSPT-T）现存放于厦门大学药学院天然产物化学研究中心。

2 提取与分离

将小叶山葡萄的干粉（5.5 kg）用 8 倍量 60%乙醇进行加热回流 3 次，每次 2.5 h，提取液浓缩得到浸膏 600 g。浸膏以大孔树脂为填料依次采用水，20%、60%、95%乙醇梯度洗脱得到 4 个馏份 V0～V3，其中 V2 经硅胶柱色谱，以氯仿-甲醇为洗脱剂分离得到 11 个馏份 V2-A～V2-K，V2-D 馏份以氯仿-甲醇为流动相，采用柱色谱方法，以薄层色谱硅胶 GF254 为填料进行分离，得到化合物 **1**（40 mg）。V2-E 馏份再经过薄层硅胶柱色谱法得到 8 个馏份 V2-E1～V2-E8，其中对 V2-E6 馏份采用反相 ODS 硅胶柱色谱得到 7 组馏份 V2-E6-1～V2-E6-7。V2-E6-2 馏份经制备 HPLC 法，以 30%色谱乙腈为流动相分离得到单体化合物 **2**（86 mg）。对 V2-F 馏份采取柱色谱手段得到 7 个馏份 V2-F1～V2-F7，其中 V2-F3 馏份采用反相 ODS 硅胶色谱进行分离得到 6 个馏份 V2-F3-A～V2-F3-F，其中 V2-F3-C 馏份采用 HPLC 法，以 25%色谱乙腈为流动相制备得到单体化合物 **5**（15 mg）和 **7**（22 mg），V2-F4 馏份采用反相 ODS 硅胶色谱进行分离得到 7 组馏份 V2-F4-A～V2-F4-G，对 V2-F4-A 馏份采用 HPLC 法，以 13%色谱乙腈为流动相制备得到化合物 **12**，对 V2-F4-E 馏份采用 HPLC 法，以 17%色谱乙腈为流动相制备得到化合物 **3**（12 mg）和 **4**（9 mg），对 V2-F4-F 馏份采用 HPLC 法，以 20%色谱乙腈为流动相制备得到化合物 **8**（11 mg）和 **11**（16 mg），对 V2-F4-G 馏份采用 HPLC 法，以 45%色谱甲醇为流动相制备得到化合物 **6**（8 mg）和 **10**（14 mg），V2-F5 馏份采用反相 ODS 硅胶色谱进行分离得到 5 组馏份 V2-F5-A～V2-F5-E，其中对 V2-F5-C 馏份采用 HPLC 法，以 30%色谱甲醇为流动相制备得到化合物 **9**（10 mg）。

3 结构鉴定

化合物 **1**：白色晶体（丙酮），ESI-MS *m*/*z* 227 [M－H]$^-$。^{1}H-NMR (400 MHz, CD_3COCD_3) δ: 7.43 (2H, d, *J* = 8.8 Hz, H-2′, 6′), 7.03 (1H, d, *J* = 16.4 Hz, H-8), 6.90 (1H, d, *J* = 16.4 Hz, H-7), 6.86 (2H, d, *J* = 8.8 Hz, H-3′, 5′), 6.58 (2H, d, *J* = 2.0 Hz, H-2, 6), 6.31 (1H, t, *J* = 2.0 Hz, H-4)；^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 159.4 (C-3, 4), 158.0 (C-4′), 140.8 (C-1), 129.8 (C-1′), 129.1 (C-8), 128.6 (C-2′, 6′), 126.7 (C-7), 116.2 (C-3′, 5′), 105.6 (C-2, 6), 102.5 (C-4)。以上数据与文献报道一致[2,4]，故鉴定化合物 **1** 为白藜芦醇。

化合物 **2**：黄色粉末，ESI-MS *m*/*z*: 453 [M－H]$^-$。^{1}H-NMR (400 MHz, CD_3COCD_3) δ: 7.19 (2H, d, *J* = 8.8 Hz, H-2′, 6′), 7.15 (2H, d, *J* = 8.8 Hz, H-2, 6), 6.89 (1H, d, *J* = 16.4 Hz, H-8), 6.82 (2H, d, *J* = 8.8 Hz, H-3′, 5′), 6.73 (2H, d, *J* = 8.8 Hz, H-3, 5), 6.72 (1H, brs, H-12), 6.69 (1H, d, *J* = 16.4 Hz, H-7), 6.33 (1H, brs, H-14), 6.23 (3H, s, H-10′, 12′, 14′), 5.42 (1H, d, *J* = 6.4 Hz, H-7′), 4.47 (1H, d, *J* = 5.2 Hz, H-8′)；^{13}C-NMR (100 MHz, CD_3OD) δ: 162.8 (C-11), 160.0 (C-11′, 13′), 159.9 (C-4′), 159.6 (C-4), 158.4 (C-13), 147.5 (C-9′), 136.8 (C-9), 133.8 (C-1′), 130.5 (C-8), 130.1 (C-1), 128.9 (C-2, 6), 128.3 (C-2′, 6′), 123.6 (C-7), 120.0 (C-10), 116.5 (C-3, 5), 116.3 (C-3′, 5′), 107.0 (C-10′, 14′), 104.3 (C-14), 102.0 (C-12′), 96.8 (C-12), 94.2 (C-7′), 57.3 (C-8′)。以上数据与文献报道一致[2,5]，故鉴定化合物 **2** 为 *trans*-ε-viniferin。

化合物 **3**：白色粉末，ESI-MS *m*/*z*: 591 [M＋Na]$^+$。^{1}H-NMR (400 MHz, CD_3OD) δ: 7.16 (1H, d, *J* = 2.0 Hz, H-2), 6.90 (1H, dd, *J* = 8.4, 1.6 Hz, H-6), 6.82 (1H, d, *J* = 2.0 Hz, H-2′), 6.78 (1H, d, *J* = 8.0 Hz,

H-5), 6.77 (1H, d, *J* = 8.0 Hz, H-5′), 6.65 (1H, dd, *J* = 8.4, 1.6 Hz, H-6′), 5.21 (1H, d, *J* = 4.0 Hz, H-7), 4.34 (1H, ddd, *J* = 8.0, 4.0, 4.0 Hz, H-8), 4.13 (1H, d, *J* = 7.6 Hz, H-1″), 3.87 (1H, dd, *J* = 11.6, 5.6 Hz, H-9a), 3.86 (1H, dd, *J* = 9.6, 2.4 Hz, H-6″a), 3.84 (1H, dd, *J* = 11.6, 5.6 Hz, H-9b), 3.83 (3H, s, 3-OCH_3), 3.82 (3H, s, 3′-OCH_3), 3.70 (1H, dd, *J* = 9.6, 2.4 Hz, H-6″b), 3.52 (2H, dd, *J* = 2.8, 6.0 Hz, H-9′), 3.33～3.27 (3H, m, H-3″, 4″, 5″), 3.16 (1H, m, H-2″), 2.60 (2H, dd, *J* = 7.6, 7.6 Hz, H-7′), 1.84～1.77 (2H, m, H-8′); ^{13}C-NMR (100 MHz, CD_3OD) *δ*: 151.5 (C-3′), 149.1 (C-3), 147.7 (C-4), 147.5 (C-4′), 138.0 (C-1′), 130.4 (C-1), 122.0 (C-6), 121.9 (C-6′), 119.0 (C-5′), 115.9 (C-5), 113.9 (C-2′), 112.8 (C-2), 101.1 (C-1″), 86.4 (C-8), 78.0 (C-7), 77.9 (C-3″), 77.8 (C-5″), 75.2 (C-2″), 71.9 (C-4″), 62.9 (C-9), 62.3 (C-6″), 62.0 (C-9′), 56.6 (C-3), 56.5 (C-3′), 35.6 (C-8′), 32.7 (C-7′)。以上数据与文献报道一致[6]，故鉴定化合物 **3** 为 (7*R*, 8*R*)-*threo*-4, 7, 9, 9′-tetrahydroxy-3, 3′-dimethoxy-8-*O*-4′-neolignan 7-*O*-β-*D*-glucopyranoside。

化合物 **4**：白色粉末，ESI-MS *m*/*z*: 545 [M＋Na]$^+$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.15 (1H, d, *J* = 8.4 Hz, H-5′), 7.05 (1H, d, *J* = 1.6 Hz, H-2′), 6.95 (1H, dd, *J* = 8.4, 1.6 Hz, H-6′), 6.75 (1H, brs, H-6), 6.73 (1H, brs, H-2), 5.52 (1H, d, *J* = 6.0 Hz, H-7′), 4.91 (1H, d, *J* = 7.6 Hz, H-1″), 3.87 (3H, s, 3-OCH_3), 3.84 (3H, s, 3′-OCH_3), 3.77 (1H, m, H-9′), 3.70 (2H, m, H-6″), 3.58 (2H, t, *J* = 6.4 Hz, H-9), 3.40～3.52 (5H, m, H-8′, 2″, 3″, 4″, 5″), 2.64 (2H, t, *J* = 7.6 Hz, H-7), 1.83 (2H, m, H-8); ^{13}C-NMR (100 MHz, CD_3OD) *δ*: 151.0 (C-3), 147.8 (C-4), 147.6 (C-4′), 145.4 (C-3′), 138.5 (C-1), 137.3 (C-1′), 129.7 (C-5′), 119.5 (C-5), 118.3 (C-6), 118.1 (C-6′), 114.4 (C-2′), 111.4 (C-2), 103.0 (C-1″), 88.6 (C-7), 78.3 (C-3″), 78.0 (C-5″), 75.1 (C-2″), 71.5 (C-4″), 65.2 (C-9), 62.7 (C-9′), 62.5 (C-6″), 57.0 (3′-OCH_3), 56.9 (3-OCH_3), 55.8 (C-8), 35.9 (C-7′), 33.0 (C-8′)。以上数据与文献报道一致[7]，故鉴定化合物 **4** 为 (7*S*, 8*R*)-urolignoside。

化合物 **5**：白色粉末，ESI-MS *m*/*z*: 515 [M＋Na]$^+$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 6.79 (1H, d, *J* = 8.0 Hz, H-5′), 6.74 (1H, s, H-5), 6.69 (1H, brs, H-2‴), 6.64 (1H, d, *J* = 8.0 Hz, H-6′), 6.17 (1H, s, H-8), 4.10 (1H, d, *J* = 7.0 Hz, H-1″), 3.99 (1H, m, H-3α), 3.94 (1H, m, H-3α), 3.81 (1H, d, *J* = 7.0 Hz, H-1), 3.81 (3H, s, 6-OCH_3), 3.78 (3H, s, 3′-OCH_3), 3.75 (1H, m, H-2α), 3.68 (1H, m, H-2α), 2.81 (2H, d, *J* = 7.0 Hz, H-4), 2.05 (2H, m, H-3); ^{13}C-NMR (100 MHz, CD_3OD) *δ*: 148.9 (C-3′), 147.1 (C-6), 145.4 (C-4′), 144.7 (C-7), 138.7 (C-1′), 134.1 (C-9), 129.4 (C-10), 123.1 (C-6′), 117.2 (C-8), 116.1 (C-5′), 113.9 (C-5), 112.6 (C-2′), 105.6 (C-1″), 77.6 (C-3″), 74.7 (C-2″), 71.0 (C-4″), 69.9 (C-2α), 66.5 (C-5″), 65.1 (C-3α), 56.6 (6-OCH_3), 56.5 (3′-OCH_3), 47.7 (C-1), 45.6 (C-2), 39.5 (C-3), 33.5 (C-4)。以上数据与文献报道一致[8]，故鉴定化合物 **5** 为 schizandriside。

化合物 **6**：黄色固体（甲醇），ESI-MS *m*/*z*: 905 [M－H]$^-$。^{1}H-NMR (400 MHz, CD_3COCD_3) *δ*: 7.18 (2H, d, *J* = 2.0, 8.4 Hz, H-2′, 6′); 7.14 (2H, d, *J* = 8.4 Hz, H-2‴, 6‴), 7.03 (2H, d, *J* = 8.0 Hz, H-2⁗, 6⁗), 6.86 (1H, dd, *J* = 8.4, 2.4 Hz, H-6″), 6.82 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 6.77 (2H, d, *J* = 8.4 Hz, H-3‴, 5‴), 6.70 (1H, d, *J* = 8.4 Hz, H-5″), 6.65 (2H, d, *J* = 8.4 Hz, H-3⁗, 5⁗), 6.50 (1H, d, *J* = 2.0 Hz, H-14″), 6.38 (2H, brs, H-7″, 8″), 6.26 (1H, d, *J* = 2.0 Hz, H-12″), 6.22 (1H, d, *J* = 2.0 Hz, H-14‴), 6.21 (1H, d, *J* = 2.0 Hz, H-12′), 6.16 (2H, d, *J* = 2.0 Hz, H-10′, 14′), 6.08 (1H, d, *J* = 2.0 Hz, H-2″), 6.06 (1H, d, *J* = 2.0 Hz, H-12⁗), 6.04 (1H, d, *J* = 2.0 Hz, H-14⁗), 6.03 (1H, d, *J* = 2.0 Hz, H-12‴), 5.87 (1H, d, *J* = 11.6 Hz, H-7‴), 5.47 (1H, d, *J* = 5.6 Hz, H-8⁗), 5.38 (1H, d, *J* = 3.2 Hz, H-7⁗), 5.35 (1H, d, *J* = 3.2 Hz, H-7′), 4.40 (1H, d, *J* = 5.6 Hz, H-8′), 4.20 (1H, d, *J* = 11.6 Hz, H-8‴); ^{13}C-NMR (100 MHz, CD_3OD) *δ*: 162.7 (C-11‴), 160.4 (C-11⁗), 159.9 (C-11′, 13′), 159.6 (C-4⁗), 158.8 (C-13‴, 11‴), 158.6 (C-13″), 158.5 (C-4′), 156.9 (C-13⁗), 155.9 (C-4‴), 155.6 (C-4″), 147.3 (C-9′), 142.6 (C-9⁗), 141.7 (C-9‴), 137.3 (C-9″), 136.1 (C-1‴), 134.1 (C-1′), 133.0 (C-3″), 132.8 (C-2″), 131.4 (C-8″), 131.2 (C-1⁗), 130.3 (C-2⁗, 6⁗), 129.4 (C-1″), 129.2 (C-2‴, 6‴), 128.2 (C-2′, 6′), 123.7 (C-6″), 122.6 (C-7″), 121.2 (C-10‴), 121.1 (C-10⁗), 119.5 (C-10″), 116.2 (C-3′, 5′, 3″, 5″), 116.2 (C-3⁗, 5⁗), 115.6 (C-3‴, 5‴), 110.5 (C-14‴), 107.5 (C-10′, 14′), 104.8 (C-14⁗), 104.5 (C-14″), 102.3 (C-12′), 101.0 (C-12⁗), 96.6 (C-12″), 96.2 (C-12‴), 94.8 (C-7′), 89.1 (C-7⁗), 58.2 (C-8′), 49.8

(C-8‴), 41.7 (C-8‴), 41.2 (C-7‴)。以上数据与文献报道一致[2]，故鉴定化合物 **6** 为 vitisin A。

化合物 **7**：黄色粉末，ESI-MS *m*/*z*: 905 [M－H]⁻。^{1}H-NMR (400 MHz, CD_3COCD_3) *δ*: 7.27 (2H, d, *J* = 8.4 Hz, H-2′, 6′), 7.21 (2H, d, *J* = 8.4 Hz, H-2‴, 6‴), 7.03 (1H, dd, *J* = 8.4, 1.6 Hz, H-6″), 6.91 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 6.84 (2H, d, *J* = 8.4 Hz, H-3‴, 5‴), 6.78 (1H, d, *J* = 16.0 Hz, H-8″), 6.70～6.62 (5H, m, H-5″, 2″, 14″, 2‴, 6‴), 6.60 (1H, d, *J* = 16.0 Hz, H-7″), 6.58 (2H, d, *J* = 8.6 Hz, H-3‴, 5‴), 6.31 (1H, d, *J* = 1.2 Hz, H-12‴), 6.26～6.20 (5H, m, H-12″, 10‴, 14‴, 12‴, 14‴), 6.20 (1H, t, *J* = 2.4 Hz, H-12′), 6.12 (2H, d, *J* = 2.4 Hz, H-10′, 14′), 5.54 (1H, d, *J* = 4.8 Hz, H-7‴), 5.42 (2H, m, H-7‴, 7′), 4.53 (1H, d, *J* = 4.8 Hz, H-8′), 4.46 (1H, d, *J* = 5.2 Hz, H-8‴), 4.32 (1H, d, *J* = 4.8 Hz, H-8‴)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 161.8 (C-11″), 161.7 (C-11‴), 159.6 (C-13‴), 159.2 (C-4″), 159.1 (C-11′, 13′), 159.0 (C-11‴, 13‴), 158.7 (C-13″), 157.5 (C-4‴), 157.4 (C-4′), 146.3 (C-4‴), 141.5 (C-9′), 136.3 (C-9‴), 134.3 (C-9‴), 134.2 (C-9″), 133.7 (C-1′), 132.9 (C-1‴), 131.8 (C-1″, 1‴), 131.4 (C-3″), 129.6 (C-8″), 127.3 (C-2‴, 6‴), 126.9 (C-2‴, 6‴), 126.8 (C-2′, 6′), 125.8 (C-6″), 124.5 (C-2″), 123.3 (C-7″), 119.2 (C-10″), 119.1 (C-10‴), 115.6 (C-3′, 5′), 115.4 (C-3‴, 5‴), 115.1 (C-3‴, 5‴), 109.7 (C-5″), 106.7 (C-10‴, 14‴), 106.6 (C-14‴), 106.1 (C-10′, 14′), 103.8 (C-14″), 101.6 (C-12′), 101.4 (C-12‴), 96.0 (C-12″), 95.8 (C-12‴), 93.9 (C-7‴), 93.8 (C-7′), 91.3 (C-7‴), 57.2 (C-8‴), 57.0 (C-8′), 52.0 (C-8‴)。以上数据与文献报道一致[2]，故鉴定化合物 **7** 为 vitisin B。

化合物 **8**：白色粉末，ESI-MS *m*/*z*: 679 [M－H]⁻。^{1}H-NMR (400 MHz, CD_3COCD_3) *δ*: 7.22 (2H, d, *J* = 8.8 Hz, H-2′, 6′), 7.05 (2H, d, *J* = 8.8 Hz, H-2″, 6″), 6.79 (2H, d, *J* = 8.8 Hz, H-3′, 5′), 6.76 (2H, d, *J* = 8.3 Hz, H-2‴, 6‴), 6.62 (2H, d, *J* = 8.3 Hz, H-3‴, 5‴), 6.60 (2H, d, *J* = 8.8 Hz, H-3″, 5″), 6.45 (1H, brs, H-14′), 6.44 (1H, brs, H-12′), 6.40 (2H, d, *J* = 2.9 Hz, H-10‴, 14‴), 6.16 (1H, t, *J* = 2.9 Hz, H-12‴), 6.09 (1H, d, *J* = 2.8 Hz, H-7′), 6.03 (1H, s, H-12″), 5.30 (1H, brs, H-7″), 4.43 (1H, d, *J* = 10.0 Hz, H-7‴), 4.41 (1H, d, *J* = 2.8 Hz, H-8′), 4.24 (1H, d, *J* = 11.6 Hz, H-8″), 3.00 (1H, dd, *J* = 11.6, 10.0 Hz, H-8‴)；^{13}C-NMR (100 MHz, CD_3COCD_3) *δ*: 158.9 (C-11″), 158.2 (C-11‴, 13‴), 158.0 (C-4″), 157.6 (C-11′), 156.4 (C-13′), 155.8 (C-4‴), 155.1 (C-4′), 154.2 (C-13‴), 146.8 (C-9′), 143.9 (C-9‴), 143.1 (C-9″), 137.4 (C-1″), 134.5 (C-1′), 134.0 (C-1‴), 129.5 (C-2‴, 6‴), 129.1 (C-2″, 6″), 127.3 (C-2′, 6′), 122.3 (C-14″), 118.8 (C-10″), 117.9 (C-10′), 115.5 (C-3′, 5′), 114.9 (C-3‴, 5‴), 114.8 (C-3″, 5″), 108.1 (C-10‴, 14‴), 103.0 (C-14′), 101.3 (C-12‴), 100.7 (C-12′), 95.6 (C-12″), 85.8 (C-7′), 67.4 (C-8‴), 56.5 (C-7‴), 51.2 (C-8″), 50.3 (C-8′), 36.4 (C-7″)。以上数据与文献报道一致[9]，故鉴定化合物 **8** 为 davidiol A。

化合物 **9**：白色粉末，ESI-MS *m*/*z*: 389 [M－H]⁻。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.46 (2H, d, *J* = 8.6 Hz, H-2′, 6′), 7.09 (2H, d, *J* = 8.6 Hz, H-3′, 5′), 7.03 (1H, d, *J* = 16.0 Hz, H-8), 6.89 (1H, d, *J* = 16.0 Hz, H-7), 6.49 (2H, brs, H-2, 6), 6.20 (1H, brs, H-4), 4.90 (1H, d, *J* = 7.6 Hz, H-1″), 3.92 (1H, dd, *J* = 12.0, 1.6 Hz, H-6″a), 3.70 (1H, dd, *J* = 12.0, 5.6 Hz, H-6″b), 3.40～3.56 (4H, m, H-2″～5″)；^{13}C-NMR (CD_3OD, 100 MHz) *δ*: 159.0 (C-3, 5), 157.5 (C-4′), 139.4 (C-1), 128.7 (C-8), 128.3 (C-1′), 128.1 (C-2′, 6′), 125.4 (C-7), 115.8 (C-3′, 5′), 107.3 (C-6), 104.9 (C-2), 102.9 (C-4), 100.8 (C-1″), 77.2 (C-3″), 76.9 (C-5″), 73.5 (C-2″), 70.0 (C-4″), 60.8 (C-6″)。以上数据与文献报道一致[10]，故鉴定化合物 **9** 为 3, 5, 4′-trihydroxystilbene 4′-*O*-β-*D*-glucopyranoside。

化合物 **10**：黄色固体，ESI-MS *m*/*z*: 679 [M－H]⁻。^{1}H-NMR (400 MHz, CD_3COCD_3) *δ*: 7.26 (2H, d, *J* = 8.8 Hz, H-2″, 6″), 7.18 (2H, d, *J* = 8.4 Hz, H-2′, 6′), 7.01 (2H, d, *J* = 8.8 Hz, H-2‴, 6‴), 6.80 (2H, d, *J* = 8.8 Hz, H-3″, 5″), 6.73 (2H, d, *J* = 8.8 Hz, H-3‴, 5‴), 6.68 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 6.35 (1H, d, *J* = 2.4 Hz, H-12″), 6.18 (2H, d, *J* = 2.0 Hz, H-10‴, 14‴), 6.17 (1H, t, *J* = 2.0 Hz, H-12‴), 6.16 (1H, d, *J* = 2.0 Hz, H-14″), 6.15 (1H, s, H-12′), 5.83 (1H, d, *J* = 11.6 Hz, H-7″), 5.27 (1H, d, *J* = 3.6 Hz, H-7′), 4.46 (1H, d, *J* = 11.6 Hz, H-8″), 4.24 (1H, d, *J* = 9.2 Hz, H-7‴), 3.76 (1H, dd, *J* = 11.6, 9.2 Hz, H-8‴), 3.63 (1H, d, *J* = 11.6 Hz, H-8′)；^{13}C-NMR (100 MHz, CD_3COCD_3) *δ*: 159.0 (C-11‴), 158.5 (C-11″, 13″), 158.4 (C-13‴), 156.4 (C-4″), 156.3 (C-4′), 155.8 (C-4‴), 155.3 (C-13′), 154.4 (C-11′), 147.0 (C-9‴), 144.3 (C-9′),

141.5 (C-9″), 133.6 (C-1′), 132.9 (C-1‴), 130.4 (C-2′, 6′), 130.3 (C-1″), 130.0 (C-2″, 6″), 129.8 (C-2‴, 6‴), 125.4 (C-10″), 121.1 (C-14′), 116.1 (C-10′), 115.8 (C-3″, 5″), 115.6 (C-3‴, 5‴), 115.1 (C-3′, 5′), 107.4 (C-10‴, 14‴), 105.4 (C-14″), 101.3 (C-12‴), 101.1 (C-12″), 96.3 (C-12′), 90.7 (C-7‴), 62.4 (C-8‴), 57.9 (C-7‴), 52.3 (C-8′), 49.4 (C-8″), 37.4 (C-7′)。以上数据与文献报道一致[2]，故鉴定化合物 **10** 为蛇葡萄素 C。

化合物 **11**：黄色粉末，ESI-MS *m*/*z*: 521 [M－H]$^-$。^{1}H-NMR (400 MHz, CD_3OD) δ: 7.01 (1H, d, J = 1.5 Hz, H-2), 6.88 (1H, dd, J = 8.0, 1.5 Hz, H-6), 6.82 (1H, brs, H-2′), 6.79 (1H, d, J = 8.0 Hz, H-5), 6.74 (1H, brs, H-6′), 5.69 (1H, d, J = 6.5 Hz, H-7), 4.38 (1H, d, J = 8.0 Hz, H-1″), 4.12 (1H, dd, J = 9.5, 5.5 Hz, H-9a), 3.86 (3H, s, 3′-OCH_3), 3.84 (3H, s, 5-OCH_3), 3.82 (1H, m, H-9b), 3.60 (2H, t, J = 10.0 Hz, H-6″a), 3.23～3.41 (7H, m, H-2″, 3″, 4″, 5″, 8, 9′a, 6″b), 2.64 (2H, t, J = 7.5 Hz, H-7′), 1.81 (2H, m, H-8′)；^{13}C-NMR (100 MHz, CD_3OD) δ: 149.2 (C-3), 147.6 (C-4′), 147.6 (C-4), 145.3 (C-3′), 137.1 (C-1′), 134.8 (C-1), 129.9 (C-5′), 119.9 (C-6), 118.4 (C-2′), 116.3 (C-5), 114.4 (C-6′), 111.1 (C-2), 104.4 (C-1″), 89.3 (C-7), 78.3 (C-2″), 78.2 (C-5″), 75.3 (C-2″), 72.5 (C-9a), 71.8 (C-4″), 62.9 (C-6″a), 62.4 (C-9′a), 56.9 (-OCH_3), 56.6 (-OCH_3), 53.1 (C-8), 35.9 (C-8′), 33.0 (C-7′)。以上数据与文献报道一致[11]，故鉴定化合物 **11** 为 (7*R*, 8*S*)-dihydrodehydrodiconiferyl alcohol 9-*O*-β-*D*-glucopyranoside。

化合物 **12**：白色粉末，ESI-MS *m*/*z*: 289 [M－H]$^-$。^{1}H-NMR (400 MHz, CD_3OD) δ: 7.00 (1H, s, H-2′), 6.82 (1H, dd, J = 2.8, 8.4 Hz, H-6′), 6.79 (1H, d, J = 8.4 Hz, H-5′), 5.97 (1H, d, J = 2.2 Hz, H-6), 5.95 (1H, d, J = 2.2 Hz, H-8), 4.83 (1H, s, H-2), 4.19 (1H, s, H-3), 2.90 (1H, dd, J = 4.4, 16.4 Hz, H-4α), 2.75 (1H, dd, J = 3.4, 16.4 Hz, H-4β)；^{13}C-NMR (100 MHz, CD_3OD) δ: 156.6 (C-9), 156.2 (C-7), 156.0 (C-5), 144.5 (C-3′), 144.4 (C-4′), 130.9 (C-1′), 118.1 (C-6′), 114.6 (C-2′), 114.0 (C-5′), 98.8 (C-10), 95.1 (C-8), 94.6 (C-6), 78.5 (C-2), 66.1 (C-3), 27.9 (C-4)。以上数据与文献报道一致[12]，故鉴定化合物 **12** 为表儿茶素。

4 讨论

由于小叶山葡萄主要分布在我国台湾地区，因此目前对其研究相对较少，本研究从小叶山葡萄中分离得到了 12 个单体化合物，其中 9 个单体化合物系首次从该植物中分离，并且分离得到的化合物多为多酚类。多酚类化合物具有抗氧化，清除自由基等活性，而氧化和自由基的产生又与肿瘤[2]、阿尔茨海默病[13]等疾病具有密切的关系，因此本研究可能为阐述小叶山葡萄的民间应用提供依据。

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