

## 地稔中酚酸类化学成分研究

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**摘要:** 采用硅胶、Sephadex LH-20、ODS 柱层析等色谱技术, 从地稔 95% 乙醇提取物的乙酸乙酯萃取部位分离得到 16 个化合物。通过波谱分析并与文献数据对照方法, 将其分别鉴定为反式阿魏酰二十烷醇酯(1)、邻羟基苯甲酸(2)、香草酸(3)、对香豆酸(4)、没食子酸甲酯(5)、没食子酸乙酯(6)、原儿茶酸(7)、没食子酸(8)、3-甲氧基鞣花酸(9)、3,3'-O-二甲基鞣花酸-4-O- $\alpha$ -L-鼠李糖苷(10)、4-O-(6''-O-对-香豆酰基- $\beta$ -D-吡喃葡萄糖)-对-香豆酸(11)、2-O-(E)-咖啡酰基-1-O-对-(E)-香豆酰基- $\beta$ -D-吡喃葡萄糖(12)、1,5-二咖啡酰奎尼酸(13)、对羟基苯乙酮(14)、avicularin(15)、苍耳烯吡喃(16)。其中除化合物 8 外, 其他 15 个化合物均为首次从地稔中分离得到。

**关键词:** 地稔; 化学成分; 酚酸类

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Chemical Constituents of Phenolic Acids in *Melastoma dodecandrum*

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**Abstract:** Sixteen compounds were isolated and purified from EtOAc fraction derived from 95% ethanol extract of *Melastoma dodecandrum* Lour by silica gel, Sephadex LH-20 and ODS column chromatography. On the basis of their physico-chemical properties and spectroscopic data, these compounds were identified as eicosyl-(E)-ferulate (1), oxybenzoic acid (2), vanillic acid (3), *p*-coumaric acid (4), methyl gallate (5), ethyl gallate (6), protocatechuic acid (7), gallic acid (8), 3-O-methyl ellagic acid (9), 3,3'-O-dimethyl ellagic acid 4-O- $\alpha$ -L-rhamnopyranoside (10), 4-O-(6''-O-*p*-coumaroyl- $\beta$ -D-glucopyranosyl)-*p*-coumaric acid (11), 2-O-(E)-caffeoyl-1-O-*p*-(E)-coumaroyl- $\beta$ -D-glucopyranose (12), 1,5-di-O-caffeoylquinic acid (13), *p*-hydroxyacetophenone (14), avicularin (15), xanthienopyran (16). All of these compounds except compound 8 were obtained from *Melastoma dodecandrum* Lour for the first time.

**Key words:** *Melastoma dodecandrum* L; chemical constituents; phenolic acids

地稔为野牡丹科植物地稔(*Melastoma dodecandrum* Lour.)的全草, 分布于长江以南的贵州、福建、浙江、广西、云南等省区, 瑶族、苗族、畲族等少数民族使用较广泛<sup>[1]</sup>。民间常用于治痛经, 产后腹痛, 血崩, 带下, 便血, 痢疾, 痈肿, 疔疮。现代临床研究报道, 地稔制剂治疗消化道出血的止血功效显著<sup>[2]</sup>。周添浓等<sup>[3]</sup>证明地稔的止血作用与其含有的总酚类物质有关。唐迈等<sup>[4]</sup>也已从地稔中分离得到了没食子酸和阿魏酸等酚酸类物质。但是, 目前对地稔中酚酸类物质的研究还不够充分。为此, 本实验对地稔的化学成分进行了较系统的研究, 从

中得到 16 个酚酸类化合物。采用波谱学和理化方法, 将这些化合物分别鉴定为反式阿魏酰二十烷醇酯(1)、邻羟基苯甲酸(2)、香草酸(3)、对香豆酸(4)、没食子酸甲酯(5)、没食子酸乙酯(6)、原儿茶酸(7)、没食子酸(8)、3-甲氧基鞣花酸(9)、3,3'-O-二甲基鞣花酸-4-O- $\alpha$ -L-鼠李糖苷(10)、4-O-(6''-O-对-香豆酰基- $\beta$ -D-吡喃葡萄糖)-对-香豆酸(11)、2-O-(E)-咖啡酰基-1-O-对-(E)-香豆酰基- $\beta$ -D-吡喃葡萄糖(12)、1,5-二咖啡酰奎尼酸(13)、对羟基苯乙酮(14)、avicularin(15)、苍耳烯吡喃(16)。

## 1 仪器与材料

Bruker AVANCEIII 300 型核磁共振光谱仪(瑞士 Bruker 公司); Finnigan LCQ Advantage MAX 质谱仪(美国 Thermo 公司); UltiMate 3000 高效液相色谱

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仪(法国 Gilson 公司), Agilent 1200 型液相半制备色谱仪, Welch Material Column XB-C<sub>18</sub> 分析色谱柱(4.6 × 250 mm, 5 μm, 上海月旭材料科技有限公司); Ultimate® XB-C<sub>18</sub> 制备色谱柱(10 × 250 mm, 5 μm, 上海月旭材料科技有限公司); Sephadex LH-20 葡聚糖凝胶(美国 Pharmacia 公司); 薄层色谱硅胶预涂板(HSAF254, 200 × 200 mm, 烟台市化学工业研究所); ODS(50 mm, YMC, 德国 Merck 公司)。

实验用药材于 2013 年 5 月采自广东省从化市, 经暨南大学生药学教研室周光雄教授鉴定为野牡丹科植物地稔(*Melastoma dodecandrum* Lour.) 的全草。

## 2 分离与纯化

地稔全草 30 kg 粉碎, 用 95% 乙醇回流提取三次。提取液减压浓缩后得粗浸膏 1210 g, 用适量水混悬, 依次用石油醚、乙酸乙酯萃取, 分别得到石油醚萃取物(430 g)、乙酸乙酯萃取物(148 g)。

将乙酸乙酯部位经硅胶柱色谱, 以氯仿-甲醇(100:0 ~ 0:100) 系统梯度洗脱, 经 TLC 薄层分析后合并浓缩, 得到 4 个组分(A1 ~ A4)。A1 组分继续经硅胶柱色谱, 以石油醚-乙酸乙酯(100:0-1:1) 系统梯度洗脱, 反复分离纯化得到化合物 **1**(173 mg)、**2**(2 mg)、**3**(10 mg) 和 **4**(22 mg)。A2 组分经硅胶柱色谱, 以氯仿-丙酮(100:0 ~ 0:100) 系统梯度洗脱, 重结晶得到化合物 **8**(506 mg), 其他子馏分经过 Sephadex LH-20 凝胶柱色谱及半制备-HPLC, 得到化合物 **5**(84 mg)、**6**(4 mg) 和 **7**(360 mg)。A3 组分经反相 ODS 开放柱色谱, 以甲醇-水(3:7-10:0) 系统梯度洗脱得到三个组分(A3B ~ A3D), A3B 和 A3C 经 Sephadex LH-20 凝胶柱色谱, 以氯仿-甲醇(1:1) 系统洗脱, 分别得到化合物 **9**(17 mg)、**10**(16 mg) 和 **11**(61 mg), A3D 经过 Sephadex LH-20 凝胶柱色谱及半制备-HPLC, 得到化合物 **12**(12 mg) 和 **13**(13 mg)。A4 组分经硅胶柱色谱, 以氯仿-丙酮(100:0 ~ 1:1) 系统梯度洗脱, 子馏分经过 Sephadex LH-20 凝胶柱色谱得到化合物 **14**(10 mg)、**15**(21 mg) 和 **16**(5 mg)。

## 3 结构鉴定

**化合物 1 白色粉末** 分子式为 C<sub>30</sub>H<sub>50</sub>O<sub>4</sub>, ESI-MS  $m/z$ : 473 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.59 (1H, d,  $J$  = 15.9 Hz, H-8), 7.04 (1H, dd,  $J$  = 8.2, 1.8 Hz, H-6), 7.00 (1H, d,  $J$  = 1.8 Hz, H-

2), 6.89 (1H, d,  $J$  = 8.1 Hz, H-5), 6.27 (1H, d,  $J$  = 15.9 Hz, H-7), 4.16 (2H, t,  $J$  = 6.6 Hz, H-1'), 3.89 (3H, s, OCH<sub>3</sub>), 1.62 ~ 1.72 (2H, m, H-2'), 1.19 (34H, br s, H-3' ~ 19'), 0.84 (3H, t,  $J$  = 6.0 Hz, H-20'); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 167.6 (C-9), 148.1 (C-3), 146.9 (C-4), 144.8 (C-7), 127.1 (C-1), 123.1 (C-6), 115.7 (C-5), 114.9 (C-8), 109.4 (C-2), 64.8 (C-1'), 56.0 (-OCH<sub>3</sub>), 32.1 (C-2'), 29.8 ~ 22.8 (C-3' ~ C-19'), 14.2 (C-20')。以上数据与文献报道一致<sup>[5]</sup>, 故化合物 **1** 鉴定为反式阿魏酰二十烷醇酯。

**化合物 2 白色粉末** 分子式为 C<sub>7</sub>H<sub>6</sub>O<sub>3</sub>, ESI-MS  $m/z$ : 137 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.90 (1H, dd,  $J$  = 8.0, 1.7 Hz, H-6), 7.50 (2H, dt,  $J$  = 8.3, 1.4 Hz, H-5), 6.98 (1H, d,  $J$  = 8.4 Hz, H-3), 6.91 (2H, t,  $J$  = 8.4 Hz, H-4); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 174.2 (-COOH), 162.4 (C-2), 137.0 (C-6), 131.1 (C-4), 119.7 (C-10), 117.9 (C-5), 111.6 (C-3)。以上数据与文献报道一致<sup>[6]</sup>, 故化合物 **2** 鉴定为邻羟基苯甲酸。

**化合物 3 白色粉末** 分子式为 C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>, ESI-MS  $m/z$ : 167 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 7.56 (1H, dd,  $J$  = 8.7, 1.9 Hz, H-6), 7.54 (1H, d,  $J$  = 1.8 Hz, H-2), 6.88 (1H, d,  $J$  = 8.7 Hz, H-5), 3.89 (3H, s, H-8); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ: 170.2 (C=O), 152.8 (C-3), 148.8 (C-4), 125.4 (C-6), 123.3 (C-1), 116.0 (C-5), 113.9 (C-2), 56.5 (-OCH<sub>3</sub>)。以上数据与文献报道一致<sup>[7]</sup>, 故化合物 **3** 鉴定为香草酸。

**化合物 4 白色粉末** 分子式为 C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>, ESI-MS  $m/z$ : 163 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 7.60 (1H, d,  $J$  = 15.9 Hz, H-3), 7.42 (2H, d,  $J$  = 8.6 Hz, H-6, 8), 6.80 (2H, d,  $J$  = 8.6 Hz, H-5, 9), 6.27 (1H, d,  $J$  = 15.9 Hz, H-2); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ: 171.3 (C-1), 161.2 (C-7), 146.8 (C-3), 131.2 (C-5, 9), 127.4 (C-4), 116.9 (C-6, 8), 115.7 (C-2)。以上数据与文献报道一致<sup>[8]</sup>, 故化合物 **4** 鉴定为对香豆酸。

**化合物 5 白色粉末** 分子式为 C<sub>8</sub>H<sub>8</sub>O<sub>5</sub>, ESI-MS  $m/z$ : 183 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 7.06 (2H, s, H-2, 6), 3.78 (3H, s, -OCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ: 169.3 (C-7), 146.3 (C-3, 5), 139.7 (C-4), 121.4 (C-1), 110.2 (C-2, 6), 52.6

(C-8)。以上数据与文献报道一致<sup>[9]</sup>,故化合物 **5** 鉴定为没食子酸甲酯。

**化合物 6 白色粉末** 分子式为  $C_9H_{10}O_5$ , ESI-MS  $m/z$ : 197 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.04 (2H, s, H-2, 6), 4.27 (2H, q,  $J = 7.1$  Hz, H-8), 1.34 (3H, t,  $J = 7.1$  Hz, H-9); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 168.7 (C-7), 146.6 (C-3, 5), 139.8 (C-4), 121.9 (C-1), 110.1 (C-2, 6), 61.8 (C-8), 14.8 (C-9)。以上数据与文献报道一致<sup>[9]</sup>,故化合物 **6** 鉴定为没食子酸乙酯。

**化合物 7 白色粉末** 分子式为  $C_7H_6O_4$ , ESI-MS  $m/z$ : 153 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.46 (1H, s, H-2), 7.43 (1H, d,  $J = 1.9$  Hz, H-6), 6.82 (1H, d,  $J = 8.0$  Hz, H-5); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 170.3 (COOH), 151.4 (C-4), 145.9 (C-3), 123.9 (C-6), 122.9 (C-1), 117.6 (C-2), 115.7 (C-5)。以上数据与文献报道一致<sup>[10]</sup>,故化合物 **7** 鉴定为原儿茶酸。

**化合物 8 白色粉末** 分子式为  $C_7H_6O_5$ , ESI-MS  $m/z$ : 169 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.11 (2H, d,  $J = 1.4$  Hz, H-2, 6); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 170.7 (COOH), 146.2 (C-3, 5), 139.6 (C-4), 121.9 (C-1), 110.4 (C-2, 6)。以上数据与文献报道一致<sup>[10]</sup>,故化合物 **8** 鉴定为没食子酸。

**化合物 9 白色粉末** 分子式为  $C_{15}H_8O_8$ , ESI-MS  $m/z$ : 315 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 7.50 (1H, s, H-5), 7.42 (1H, s, H-5'), 4.02 (3H, s, -OMe); <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ )  $\delta$ : 159.0 (C-7), 158.8 (C-7'), 152.1 (C-4), 148.4 (C-4'), 141.5 (C-3'), 140.1 (C-2), 136.1 (C-2'), 112.5 (C-1'), 112.2 (C-6), 111.9 (C-5'), 111.3 (C-1), 110.1 (C-5), 106.6 (C-6'), 60.9 (OMe)。以上数据与文献报道一致<sup>[11]</sup>,故化合物 **9** 鉴定为 3-甲氧基鞣花酸。

**化合物 10 白色粉末** 分子式为  $C_{22}H_{20}O_{12}$ , ESI-MS  $m/z$ : 475 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 7.63 (1H, s, H-5), 7.33 (1H, s, H-5'), 5.52 (1H, d,  $J = 1.6$  Hz, H-1''), 4.05 (3H, s, -OMe), 3.99 (1H, dd,  $J = 3.3, 9.0$  Hz, H-2''), 3.71 (1H, dd,  $J = 3.0, 9.2$  Hz, H-3''), 3.49 ~ 3.56 (1H, m, H-5''), 1.16 (3H, d,  $J = 6.1$  Hz, H-6''); <sup>13</sup>C NMR (75 MHz, DM-

SO- $d_6$ )  $\delta$ : 158.1 (C-7'), 157.9 (C-7), 152.8 (C-4'), 150.3 (C-4), 141.6 (C-2'), 141.2 (C-2), 140.7 (C-3), 140.0 (C-3'), 113.5 (C-6), 112.2 (C-6'), 111.6 (C-1'), 111.5 (C-1), 111.3 (C-5), 110.5 (C-5'), 99.8 (C-1''), 71.6 (C-4''), 70.5 (C-2''), 70.3 (C-3''), 70.1 (C-5''), 61.5 (OMe), 60.9 (OMe), 18.0 (C-6'')。以上数据与文献报道一致<sup>[12]</sup>,故化合物 **10** 鉴定为 3,3'-*O*-二甲基鞣花酸-4-*O*- $\alpha$ -*L*-鼠李糖苷。

**化合物 11 白色粉末** 分子式为  $C_{24}H_{24}O_{10}$ , ESI-MS  $m/z$ : 471 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.62 (1H, d,  $J = 15.9$  Hz, H-7), 7.52 (1H, d,  $J = 15.9$  Hz, H-7'), 7.48 (1H, d,  $J = 8.7$  Hz, H-2, 6), 7.45 (1H, d,  $J = 8.6$  Hz, H-2', 6'), 7.09 (1H, d,  $J = 8.7$  Hz, H-3, 5), 6.82 (1H, d,  $J = 8.6$  Hz, H-3', 5'), 6.35 (1H, d,  $J = 15.9$  Hz, H-8), 6.23 (1H, d,  $J = 15.9$  Hz, H-8'), 4.98 (1H, d,  $J = 7.2$  Hz, H-1''), 4.55 (1H, dd,  $J = 3.2, 11.9$  Hz, H-6''a), 4.36 (1H, dd,  $J = 7.2, 11.9$  Hz, H-6''b), 3.73 ~ 3.79 (1H, m, H-5''), 3.49 ~ 3.55 (1H, m, H-2''), 3.50 (1H, d,  $J = 2.5$  Hz, H-3''), 3.38 ~ 3.44 (1H, m, H-4''); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 170.8 (C-9), 169.0 (C-9'), 161.6 (C-4'), 160.7 (C-4), 147.0 (C-7'), 145.8 (C-7), 131.4 (C-2', 6'), 130.9 (C-2, 6), 130.1 (C-1), 127.2 (C-1'), 118.2 (C-8'), 117.7 (C-3, 5), 117.1 (C-3', 5'), 115.1 (C-8), 101.8 (C-1''), 78.0 (C-3''), 75.7 (C-5''), 74.9 (C-2''), 72.0 (C-4''), 64.8 (C-6'')。以上数据与文献报道一致<sup>[13]</sup>,故化合物 **11** 鉴定为 4-*O*-(6''-*O*-对-香豆酰基- $\beta$ -*D*-吡喃葡萄糖)-对-香豆酸。

**化合物 12 白色粉末** 分子式为  $C_{24}H_{24}O_{11}$ , ESI-MS  $m/z$ : 487 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.73 [1H, d,  $J = 15.8$  Hz, coumaroyl (H-7<sub>co</sub>)], 7.57 (1H, d,  $J = 15.8$  Hz, H-7<sub>caf</sub>), 7.47 (2H, d,  $J = 8.0$  Hz, H-2<sub>co</sub>, 6<sub>co</sub>), 7.06 (1H, d,  $J = 2$  Hz, H-2<sub>caf</sub>), 6.95 (1H, dd,  $J = 2, 8$  Hz, H-6<sub>caf</sub>), 6.81 (2H, d,  $J = 7.9$  Hz, H-3<sub>co</sub>, 5<sub>co</sub>), 6.37 (1H, d,  $J = 8$  Hz, H-5<sub>caf</sub>), 6.29 (1H, d,  $J = 15.9$  Hz, H-8<sub>caf</sub>), 6.27 (1H, d,  $J = 15.9$  Hz, H-8<sub>co</sub>), 5.60 (1H, d,  $J = 8.0$  Hz, glc H-1), 4.50 (1H, br d, glc H-2), 4.32 (1H, d,  $J = 11.4$  Hz, glc H-6), 3.68 (1H, t,  $J = 9.0$  Hz, glc H-3), 3.45 ~ 3.52 (2H, m, glc H-4, 5); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : caffeoyl-127.9 (C-1), 114.9 (C-2),

146.9 (C-3), 149.7 (C-4), 116.6 (C-5), 123.2 (C-6), 148.2 (C-7), 115.3 (C-8), 169.3 (C-9); coumaroyl-127.2 (C-1), 131.6 (C-2, 6), 117.0 (C-3, 5), 161.7 (C-4), 147.5 (C-7), 114.5 (C-8), 167.8 (C-9); glucose-95.9 (C-1), 74.1 (C-2), 76.5 (C-3), 71.5 (C-4), 78.0 (C-5), 64.5 (C-6)。以上数据与文献报道一致<sup>[14]</sup>, 故化合物 **12** 鉴定为 2-*O*-(*E*)-咖啡酰基-1-*O*-对-(*E*)-香豆酰基- $\beta$ -D-吡喃葡萄糖。

**化合物 13 黄色粉末** 分子式为  $C_{25}H_{24}O_{12}$ , ESI-MS  $m/z$ : 515 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.59 (2H, d,  $J = 16$  Hz, H-8', 8''), 7.07 (2H, br s, H-2', 2''), 6.96 (2H, dd,  $J = 2.0, 8.1$  Hz, H-6', 6''), 6.78 (2H, d,  $J = 8.2$  Hz, H-5', 5''), 6.29 (2H, dd,  $J = 9.4, 15.9$  Hz, H-8', 8''), 5.36 ~ 5.42 (1H, m, H-5), 4.27 ~ 4.30 (1H, m, H-3), 3.78 (1H, dd,  $J = 3.3, 8.1$  Hz, H-4), 2.57 (1H, dd,  $J = 3.6, 13.6$  Hz, H-6), 2.43 ~ 2.46 (2H, m, H-2), 2.04 ~ 2.11 (1H, m, H-6); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 178.0 (C-7), 168.8 (C-9''), 168.2 (C-9'), 149.8 (C-4''), 149.7 (C-4'), 147.6 (C-7''), 147.4 (C-7'), 146.9 (C-3'', 3'), 127.9 (C-1'', 1'), 123.2 (C-6'', 6'), 116.6 (C-5'', 5'), 115.4 (C-8'', 8'), 115.3 (C-2'', 2'), 81.1 (C-1), 73.0 (C-4), 71.7 (C-5), 69.6 (C-3), 37.1 (C-6), 35.8 (C-2)。以上数据与文献报道一致<sup>[15]</sup>, 故化合物 **13** 鉴定为 1,5-二咖啡酰奎尼酸。

**化合物 14 无色油状物** 分子式为  $C_8H_8O_2$ , ESI-MS  $m/z$ : 271 [2M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.83 (2H, d,  $J = 7.8$  Hz, H-2', 6'), 6.77 (2H, d,  $J = 8.4$  Hz, H-3', 5'), 2.48 (3H, s, H-2); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 199.6 (C-1), 164.7 (C-4'), 132.3 (C-2', 6'), 130.0 (C-1'), 116.5 (C-3', 5'), 26.4 (C-2)。以上数据与文献报道一致<sup>[16]</sup>, 故化合物 **14** 鉴定为对羟基苯乙酮。

**化合物 15 黄色粉末** 分子式为  $C_{26}H_{34}O_{10}$ , ESI-MS  $m/z$ : 505 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$ : 6.76 (1H, d,  $J = 8.0$  Hz, H-5'), 6.70 (1H, s, H-5), 6.67 (1H, s, H-8), 6.64 (1H, s,  $J = 1.7$  Hz, H-2'), 6.59 (1H, dd,  $J = 8.0, 1.8$  Hz, H-6'), 3.84 (1H, br s, H-1), 3.81 (3H, s, -OMe), 3.77 (3H, s, -OMe), 2.83 (2H, d,  $J = 7.6$  Hz, H-4), 2.02 ~ 2.06 (3H, m, H-3), 1.86 (1H, br t,  $J = 10.1$  Hz, H-2), 4.52 (1H, d,  $J = 1.4$  Hz, H-1''), 3.88 (1H, dd,  $J =$

3.2, 1.6 Hz, H-2''), 3.65 (1H, dd,  $J = 9.5, 3.4$  Hz, H-3''), 3.49 ~ 3.54 (1H, m, H-5''), 3.35 ~ 3.38 (1H, m, H-4''), 1.19 (1H, d,  $J = 6.2$  Hz, H-6''); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$ : 149.3 (C-6), 147.4 (C-3'), 146.2 (C-7), 145.4 (C-4'), 138.2 (C-9), 134.1 (C-1'), 129.0 (C-10), 123.3 (C-6'), 117.3 (C-8), 116.2 (C-5'), 113.6 (C-2'), 112.6 (C-5), 102.4 (C-1''), 74.0 (C-4''), 72.7 (C-3''), 72.5 (C-2''), 70.3 (C-5''), 68.1 (C-2 $\alpha$ ), 65.5 (C-3 $\alpha$ ), 56.5 (6-OMe), 48.5 (C-1), 45.6 (C-2), 40.2 (C-3), 33.7 (C-4), 18.1 (C-6'')。以上数据与文献报道一致<sup>[17]</sup>, 故化合物 **15** 鉴定为 aviculin。

**化合物 16 黄色粉末** 分子式为  $C_{17}H_{16}O_4S$ , ESI-MS  $m/z$ : 315 [M-H]<sup>-</sup>。<sup>1</sup>H NMR (300 MHz, DM-SO- $d_6$ )  $\delta$ : 7.36 (1H, s, H-4), 7.05 (1H, d,  $J = 1.5$  Hz, H-3), 6.50 (1H, dd,  $J = 15.0, 10.5$  Hz, H-10), 6.17 (1H, dd,  $J = 15.0, 10.5$  Hz, H-11), 6.07 (1H, d,  $J = 6.8$  Hz, H-8), 5.90 (1H, dt,  $J = 15.0, 7.2$  Hz, H-12), 5.69 (1H, dd,  $J = 15.0, 7.2$  Hz, H-9), 3.60 (2H, t,  $J = 6.6$  Hz, H-14), 2.61 (3H, d,  $J = 1.5$  Hz, H-15), 2.30 ~ 2.33 (2H, m, H-3); <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ )  $\delta$ : 170.5 (C-6), 151.6 (C-5), 145.7 (C-3a), 145.3 (C-2), 136.0 (C-10), 135.8 (C-8a), 134.7 (C-12), 132.4 (C-11), 127.7 (C-8b), 126.2 (C-9), 121.9 (C-3), 121.3 (C-4a), 114.7 (C-4), 81.9 (C-8), 62.5 (C-14), 37.2 (C-13), 16.2 (C-15)。以上数据与文献报道一致<sup>[18]</sup>, 故化合物 **16** 鉴定为苍耳烯吡喃。

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