

黄花三宝木枝条的化学成分研究 II

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摘要: 为了解黄花三宝木(*Trigonostemon lutescens* Y. T. Chang et J. Y. Liang)的化学成分, 采用硅胶柱色谱与 Sephadex LH-20 凝胶柱色谱从黄花三宝木乙醇提取物的石油醚与正丁醇萃取部分共分离 11 个化合物, 其结构分别鉴定为: *ent*-kaurane-3 β ,16 β -diol (1)、(3*R*,6*R*,7*E*)-3-hydroxy-4,7-megastigmadien-9-one (2)、palmarumycin JC2 (3)、(\pm)-3-(3,4,5-trimethoxyphenyl)-1,2-propanediol (4)、赤式-愈创木基甘油- β -O-4'-松柏基醚 (5)、苏式-愈创木基甘油- β -O-4'-松柏基醚 (6)、3-hydroxymethyl-5-(3-hydroxypropyl)-7-methoxy-2-{3-methoxy-4-[1-(3,4-dimethoxybenzyl)-2-hydroxyethyl]phenyl}-2,3-dihydrobenzofuran (7)、ancistrocline (8)、hamatine (9)、东茛菪苷 (10)和紫丁香苷 (11)。上述化合物均为首次从该种植物中分离得到, 其中化合物 1、3~11 为首次从该属植物中分离得到。

关键词: 黄花三宝木; 枝条; 化学成分

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Chemical Constituents from Twigs of *Trigonostemon lutescens* (II)

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Abstract: In order to understand the chemical constituents of *Trigonostemon lutescens*, eleven compounds were isolated from its 95% EtOH extract by silica gel and sephadex LH-20 column chromatography. On the basis of spectral data, they were identified as *ent*-kaurane-3 β ,16 β -diol (1), (3*R*,6*R*,7*E*)-3-hydroxy-4,7-megastigmadien-9-one (2), palmarumycin JC2 (3), (\pm)-3-(3,4,5-trimethoxyphenyl)-1,2-propanediol (4), erythro-guaiacylglycerol- β -O-4'-coniferyl ether (5), threo-guaiacylglycerol- β -O-4'-coniferyl ether (6), 3-hydroxymethyl-5-(3-hydroxypropyl)-7-methoxy-2-{3-methoxy-4-[1-(3,4-dimethoxybenzyl)-2-hydroxyethyl]phenyl}-2,3-dihydrobenzofuran (7), ancistrocline (8), hamatine (9), scopolin (10), syringin (11). All the compounds were isolated from this plant for the first time, and they were isolated from the genus *Trigonostemon* for the first time except of compound 12.

Key words: *Trigonostemon lutescens*; Twigs; Chemical constituent

黄花三宝木(*Trigonostemon lutescens* Y. T. Chang et J. Y. Liang)为大戟科(Euphorbiaceae)三宝木属植物。三宝木属植物约有 50 余种, 多为灌木, 主要分布于亚洲的热带与亚热带地区, 我国共有 10 种^[1]。

黄花三宝木生于石灰岩山地的灌木林中, 为广西特有种, 分布于广西东南部。在泰国和我国, 三宝木作为民间用药, 具有化痰、止泻、防腐、杀菌等功效^[2]。据报道, 三宝木中含有瑞香烷型二萜^[3-4]、生

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物碱^[5-6]、菲类^[7]等化学成分,具有抗肿瘤^[4]、抗艾滋病病毒^[3]、杀虫^[8]等活性。本课题组前期对黄花三宝木 95% 乙醇提取物的乙酸乙酯萃取部分进行了研究^[9],从中分离得到了一类新颖骨架的生物碱^[10],为了进一步全面系统的了解其化学成分,继续对其石油醚与正丁醇萃取部分进行研究。本次研究运用多种分离纯化方法,并根据波谱数据与理化常数分析鉴定了 11 个化合物。本文报道了这些化合物的分离纯化及结构鉴定工作。

1 材料和方法

1.1 材料

黄花三宝木(*Trigonostemon lutescens* Y. T. Chang et J. Y. Liang)于 2011 年 9 月采于广西省崇左市,经中国热带农业科学院代正福副研究员鉴定,凭证标本(No. A20110901)存放于中国热带农业科学院热带生物技术研究所。

1.2 仪器和试剂

核磁数据测定采用 Bruker AV-500 型超导核磁仪(TMS 内标,瑞士 Bruker 公司);质谱测定采用 Autospec-3000 质谱仪;熔点测定采用北京泰克 X-5 型显微熔点仪测定(温度未校正);比旋光度测定采用 Autopol 旋光仪测定。薄层色谱硅胶板、柱色谱硅胶(200~300 目, 60~80 目)均为青岛海洋化工厂产品;Sephadex LH-20 填料柱为 Merck 公司产品;D-101 大孔吸附树脂购于山东鲁抗医药有限公司。提取和分离所用试剂为重蒸工业试剂。

1.3 提取和分离

黄花三宝木枝条(15.7 kg)自然晾干后粉碎,经体积分数 95% 的乙醇浸提 3 次,每次 7 d。所得滤液浓缩至无醇味,得到乙醇提取物,加水分散成悬浊液,分别用石油醚、乙酸乙酯、正丁醇各萃取 3 次,并将得到的萃取物浓缩至无溶剂,得到石油醚萃取物(87.0 g)、乙酸乙酯萃取物(52.4 g)、正丁醇萃取物(136.8 g)。

将石油醚萃取物经减压硅胶柱层析(石油醚-乙酸乙酯 1:0~0:1 梯度洗脱)得到 5 个部分 Fr.1~Fr.5。Fr.4 (6.1 g)经反复硅胶层析(以石油醚-乙酸乙酯,石油醚-丙酮为洗脱系统)和 Sephadex LH-20 凝胶柱层析(以氯仿-甲醇 1:1 为洗脱系统)分离得到

化合物 **1** (20.0 mg)、**2** (2.0 mg)和 **3** (2.0 mg)。

正丁醇萃取物(136.8 g)经大孔吸附树脂柱,甲醇洗脱,收集洗脱液并浓缩得到甲醇洗脱物(53.2 g)。经减压硅胶柱层析(氯仿-甲醇 1:0~0:1 梯度洗脱)得到 4 个部分 Fr.1~Fr.4。Fr.3 (15.0 g)经反复硅胶层析(以氯仿-丙酮,氯仿-甲醇为洗脱系统)和 Sephadex LH-20 凝胶柱层析(以氯仿-甲醇 1:1 为洗脱系统)分离得到化合物 **4** (8.0 mg)、**5** (4.0 mg)、**6** (3.0 mg)和 **7** (4.0 mg)。Fr.4 (6.1 g)经反复硅胶层析(以氯仿-甲醇为洗脱系统)再经反复 Sephadex LH-20 凝胶柱层析(以氯仿-甲醇 1:1 为洗脱系统)分离得到化合物 **8** (5.0 mg)、**9** (13.0 mg)、**10** (3.0 mg)和 **11** (4.0 mg)。

1.4 结构鉴定

ent-Kaurane-3 β ,16 β -diol (1) 无色结晶, mp 202°C~203°C; EI-MS m/z : 306 [M]⁺; ¹H NMR (500 MHz, CDCl₃): δ 3.12 (1H, dd, J = 11.1, 5.2 Hz, H-3), 1.57 (2H, m, H-2), 1.38 (3H, s, H-17), 1.04 (3H, s, H-20), 0.99 (3H, s, H-19), 0.76 (3H, s, H-18); ¹³C NMR (125 MHz, CDCl₃): δ 38.7 (C-1), 27.4 (C-2), 79.2 (C-3), 38.9 (C-4), 55.2 (C-5), 19.4 (C-6), 42.1 (C-7), 45.2 (C-8), 56.8 (C-9), 39.1 (C-10), 18.2 (C-11), 26.9 (C-12), 49.1 (C-13), 37.7 (C-14), 57.9 (C-15), 79.4 (C-16), 24.6 (C-17), 28.2 (C-18), 15.5 (C-19), 17.9 (C-20)。上述波谱数据与文献[11]报道基本一致,故鉴定此化合物为 *ent*-kaurane-3 β ,16 β -diol。

(3R,6R,7E)-3-Hydroxy-4,7-megastigmadien-9-one (2) 无色油状, [α]_D²⁵ +84.6° (c 0.3, CH₃OH); EI-MS m/z : 208 [M]⁺; ¹H NMR (500 MHz, CDCl₃): δ 6.56 (1H, dd, J = 15.8, 10.1 Hz, H-7), 6.12 (1H, d, J = 15.8 Hz, H-8), 5.65 (1H, br s, H-4), 4.29 (1H, m, H-3), 2.52 (1H, d, J = 10.1 Hz, H-6), 2.28 (3H, s, H-10), 1.86 (1H, dd, J = 13.3, 5.9 Hz, H-2b), 1.64 (3H, s, H-13), 1.39 (1H, dd, J = 13.3, 7.5 Hz, H-2a), 1.05 (3H, s, H-11), 0.91 (3H, s, H-12); ¹³C NMR (125 MHz, CDCl₃): δ 34.0 (C-1), 43.9 (C-2), 65.6 (C-3), 125.9 (C-4), 135.5 (C-5), 54.4 (C-6), 147.3 (C-7), 133.7 (C-8), 198.2 (C-9), 27.3 (C-10), 29.8 (C-11), 24.8 (C-12), 22.8 (C-13)。上述波谱数据与文献[12]报道基本一致,故鉴定此化合物为(3R,6R,7E)-3-hydroxy-4,7-megastigmadien-9-one。

Palmarumycin JC2 (3) 白色粉末, mp 192°C~194°C; [α]_D²⁵ +131.9° (c 0.5, CHCl₃); EI-MS m/z : 334

[M]⁺; ¹H NMR (500 MHz, CDCl₃): δ 12.37 (1H, br s, -OH), 7.59 (1H, t, *J* = 8.3 Hz, H-7), 7.58 (1H, d, *J* = 7.7 Hz, H-1'), 7.56 (1H, d, *J* = 8.3 Hz, H-6), 7.52 (1H, t, *J* = 7.7 Hz, H-8'), 7.47 (1H, t, *J* = 7.7 Hz, H-2'), 7.37 (1H, d, *J* = 7.7 Hz, H-3'), 7.11 (1H, d, *J* = 8.3 Hz, H-8), 7.11 (1H, d, *J* = 7.7 Hz, H-9'), 6.94 (1H, d, *J* = 7.7 Hz, H-7'), 4.62 (1H, t, *J* = 3.6 Hz, H-3), 3.27 (1H, dd, *J* = 17.7, 3.6 Hz, H-2a), 2.97 (1H, dd, *J* = 17.7, 3.6 Hz, H-2b); ¹³C NMR (125 MHz, CDCl₃): δ 201.1 (C-1), 41.4 (C-2), 67.3 (C-3), 98.8 (C-4), 138.0 (C-5), 121.2 (C-6), 137.2 (C-7), 120.0 (C-8), 162.2 (C-9), 121.6 (C-10), 109.0 (C-1'), 127.8 (C-2'), 118.1 (C-3'), 146.4 (C-4'), 113.2 (C-5'), 147.2 (C-6'), 115.4 (C-7'), 127.8 (C-8'), 109.7 (C-9'), 134.3 (C-10'). 上述波谱数据与文献[13]报道基本一致, 故鉴定化合物为 palmarumycin JC2。

(±)-3-(3,4,5-Trimethoxyphenyl)-1,2-propanediol

(4) 白色粉末, mp 71°C~72°C; [α]_D²⁵ 0.0° (*c* 2.5, CHCl₃); EI-MS *m/z*: 242 [M]⁺; ¹H NMR (500 MHz, CDCl₃): δ 6.46 (2H, s, H-2, 6), 3.97 (1H, m, H-8), 3.87 (6H, s, 3, 5-OMe), 3.84 (3H, s, 4-OMe), 3.73 (1H, dd, *J* = 11.1, 3.1 Hz, H-9b), 3.56 (1H, dd, *J* = 11.1, 6.9 Hz, H-9a), 2.77 (1H, dd, *J* = 13.7, 4.9 Hz, H-7b), 2.70 (1H, dd, *J* = 13.7, 8.4 Hz, H-7a); ¹³C NMR (125 MHz, CDCl₃): δ 136.6 (C-1), 106.2 (C-2), 153.4 (C-3), 133.6 (C-4), 153.4 (C-5), 106.2 (C-6), 40.2 (C-7), 73.1 (C-8), 66.2 (C-9), 61.0 (4-OMe), 56.2 (3, 5-OMe)。上述波谱数据与文献[14]报道基本一致, 故鉴定此化合物为(±)-3-(3,4,5-trimethoxyphenyl)-1,2-propanediol。

赤式-愈创木基甘油-β-O-4'-松柏基醚 (erythro-

Guaiacylglycerol-β-O-4'-(coniferyl alcohol) ether, 5) 黄色油状物, [α]_D²⁵ -1.7° (*c* 0.5, CH₃OH); EI-MS *m/z*: 376 [M]⁺; ¹H NMR (500 MHz, CD₃OD): δ 7.04 (1H, d, *J* = 1.5 Hz, H-2), 7.02 (1H, d, *J* = 1.5 Hz, H-2'), 7.01 (1H, d, *J* = 7.6 Hz, H-5'), 6.90 (1H, dd, *J* = 7.6, 1.5 Hz, H-6'), 6.85 (1H, dd, *J* = 7.4, 1.5 Hz, H-6), 6.75 (1H, d, *J* = 7.4 Hz, H-5), 6.52 (1H, d, *J* = 13.8 Hz, H-7'), 6.23 (1H, dt, *J* = 13.8, 6.2 Hz, H-8'), 4.90 (1H, d, *J* = 4.5 Hz, H-7), 4.40 (1H, m, H-8), 4.22 (2H, br s, H-9'), 3.86 (1H, m, H-9b), 3.84 (3H, s, 3-OMe), 3.82 (3H, s, 3'-OMe), 3.78 (1H, m, H-9a); ¹³C NMR (125 MHz, CD₃OD): δ 134.1 (C-1), 111.8 (C-2),

148.7 (C-3), 147.0 (C-4), 115.6 (C-5), 121.0 (C-6), 74.1 (C-7), 86.1 (C-8), 62.2 (C-9), 133.0 (C-1'), 111.3 (C-2'), 151.9 (C-3'), 148.8 (C-4'), 118.8 (C-5'), 120.6 (C-6'), 128.5 (C-7'), 131.5 (C-8'), 63.2 (C-9'), 56.5 (3-OMe), 56.3 (3'-OMe)。上述波谱数据与文献[15]报道基本一致, 故鉴定此化合物为赤式-愈创木基甘油-β-O-4'-松柏基醚。

苏式-愈创木基甘油-β-O-4'-松柏基醚 (threo-Guaiacylglycerol-β-O-4'-(coniferyl alcohol) ether, 6)

黄色油状物, [α]_D²⁵ +1.4° (*c* 0.5, CH₃OH); EI-MS *m/z*: 376 [M]⁺; ¹H NMR (500 MHz, CD₃OD): δ 7.10 (1H, d, *J* = 1.5 Hz, H-2), 7.10 (1H, dd, *J* = 7.8, 1.5 Hz, H-5'), 7.04 (1H, d, *J* = 1.5 Hz, H-2'), 6.93 (1H, d, *J* = 7.4 Hz, H-6), 6.90 (1H, d, *J* = 7.8 Hz, H-6'), 6.78 (1H, dd, *J* = 7.4, 1.5 Hz, H-5), 6.55 (1H, d, *J* = 13.8 Hz, H-7'), 6.28 (1H, dt, *J* = 13.8, 6.2 Hz, H-8'), 4.85 (1H, d, *J* = 5.6 Hz, H-7), 4.30 (1H, m, H-8), 4.22 (2H, br s, H-9'), 3.90 (3H, s, 3'-OMe), 3.82 (3H, s, 3-OMe), 3.70 (1H, m, H-9b), 3.49 (1H, dd, *J* = 11.8, 5.3 Hz, H-9a); ¹³C NMR (125 MHz, CD₃OD): δ 133.7 (C-1), 111.7 (C-2), 148.9 (C-3), 147.1 (C-4), 115.8 (C-5), 120.8 (C-6), 74.0 (C-7), 87.0 (C-8), 61.9 (C-9), 133.1 (C-1'), 111.2 (C-2'), 151.7 (C-3'), 149.2 (C-4'), 118.7 (C-5'), 120.7 (C-6'), 128.6 (C-7'), 131.4 (C-8'), 63.7 (C-9'), 56.3 (3-OMe), 56.5 (3'-OMe)。上述波谱数据与文献[15]报道基本一致, 故鉴定此化合物为苏式-愈创木基甘油-β-O-4'-松柏基醚。

3-Hydroxymethyl-5-(3-hydroxypropyl)-7-methoxy-2-{3-methoxy-4-[1-(3,4-dimethoxybenzyl)-2-hydroxyethyl]phenyl}-2,3-dihydrobenzofuran (7)

淡黄色液体, [α]_D²⁵ +36.0° (*c* 0.05, CD₃OH); EI-MS *m/z*: 538 [M]⁺; ¹H NMR (500 MHz, CD₃OD): δ 6.97 (1H, d, *J* = 1.8 Hz, H-2), 6.84 (1H, dd, *J* = 8.0, 1.8 Hz, H-6'), 6.77 (1H, d, *J* = 8.0 Hz, H-5'), 6.74 (1H, br s, H-6), 6.74 (1H, br s, H-2''), 6.67 (1H, s, H-5''), 6.60 (1H, d, *J* = 1.8 Hz, H-2'), 6.56 (1H, dd, *J* = 8.0, 1.8 Hz, H-6''), 5.51 (1H, d, *J* = 6.3 Hz, H-7'), 3.87 (3H, s, -OMe), 3.84 (1H, m, H-9'b), 3.83 (3H, s, -OMe), 3.83 (3H, s, -OMe), 3.77 (1H, m, H-9'a), 3.75 (3H, s, -OMe), 3.61 (2H, t, *J* = 6.6 Hz, H-9), 3.61 (2H, t, *J* = 6.6 Hz, H-9''), 3.50 (1H, m, H-8'), 2.69 (1H, dd, *J* = 6.7, 13.6 Hz, H-7''b), 2.69 (2H, br t, *J* = 7.6 Hz, H-7), 2.57 (1H, dd, *J* = 6.7, 13.6 Hz, H-7''a), 1.93 (1H, m, H-8''), 1.84

(2H, m, H-8); ^{13}C NMR (125 MHz, CD_3OD): δ 129.7 (C-1), 113.2 (C-2), 147.8 (C-3), 145.4 (C-4), 138.9 (C-5), 117.9 (C-6), 32.9 (C-7), 35.8 (C-8), 61.5 (C-9), 134.7 (C-1'), 111.5 (C-2'), 147.1 (C-3'), 122.7 (C-4'), 116.1 (C-5'), 119.7 (C-6'), 88.7 (C-7'), 55.4 (C-8'), 64.9 (C-9'), 132.8 (C-1''), 113.3 (C-2''), 147.3 (C-3''), 143.2 (C-4''), 114.0 (C-5''), 115.7 (C-6''), 36.0 (C-7''), 44.1 (C-8''), 62.0 (C-9''), 56.1 (-OMe), 56.3 (-OMe), 56.7 (-OMe), 56.8 (-OMe)。上述波谱数据与文献[16]报道基本一致,故鉴定此化合物为 3-hydroxymethyl-5-(3-hydroxypropyl)-7-methoxy-2-{3-methoxy-4-[1-(3,4-dimethoxy-benzyl)-2-hydroxyethyl] phenyl}-2,3-dihydrobenzofuran。

Ancistrocline (8) 白色粉末, mp 229°C~233°C; $[\alpha]_{\text{D}}^{25} +61.7^\circ$ (*c* 2.1, CHCl_3); EI-MS *m/z*: 421 $[\text{M}]^+$; ^1H NMR (500 MHz, CDCl_3): δ 7.21 (1H, t, *J* = 8.1 Hz, H-7'), 6.88 (1H, d, *J* = 8.1 Hz, C-6'), 6.84 (1H, s, H-3'), 6.78 (1H, d, *J* = 8.1 Hz, H-8'), 6.60 (1H, s, H-7), 3.98 (3H, s, 5'-OMe), 3.94 (3H, s, 8-OMe), 3.92 (3H, s, 4'-OMe), 3.73 (1H, m, H-1), 2.34 (3H, s, N-Me), 2.32 (1H, m, H-3), 2.16 (3H, s, 2'-Me), 2.10

(1H, m, H-4b), 1.91 (1H, m, H-4a), 1.44 (3H, d, *J* = 6.5 Hz, 1-Me), 1.06 (3H, d, *J* = 6.5 Hz, 3-Me); ^{13}C NMR (125 MHz, CDCl_3): δ 57.6 (C-1), 55.8 (C-3), 35.3 (C-4), 118.1 (C-5), 152.3 (C-6), 96.8 (C-7), 157.2 (C-8), 127.7 (C-9), 137.1 (C-10), 121.9 (C-1'), 135.7 (C-2'), 109.3 (C-3'), 157.6 (C-4'), 158.1 (C-5'), 105.0 (C-6'), 127.8 (C-7'), 116.8 (C-8'), 137.9 (C-9'), 115.7 (C-10'), 20.6 (1-Me), 20.5 (2'-Me), 21.1 (3-Me), 41.1 (N-Me), 55.9 (4'-OMe), 56.8 (5'-OMe), 55.3 (8-OMe)。上述波谱数据与文献[17]报道基本一致,故鉴定此化合物为 ancistrocline。

Hamatine (9) 白色粉末, mp 240°C~242°C; $[\alpha]_{\text{D}}^{25} +16.0^\circ$ (*c* 0.32, CHCl_3); EI-MS *m/z*: 407 $[\text{M}]^+$; ^1H NMR (500 MHz, CDCl_3): δ 7.33 (1H, t, *J* = 8.1 Hz, H-7'), 6.89 (1H, d, *J* = 8.1 Hz, H-8'), 6.80 (1H, s, H-3'), 6.83 (1H, d, *J* = 8.1 Hz, H-6'), 6.55 (1H, s, H-7), 4.84 (1H, m, H-1), 4.02 (3H, s, 5'-OMe), 3.98 (3H, s, 4'-OMe), 3.88 (3H, s, 8-OMe), 3.54 (1H, m, H-3), 2.45 (1H, m, H-4b), 2.28 (1H, m, H-4a), 2.16 (3H, s, 2'-Me), 1.75 (3H, d, *J* = 6.5 Hz, 3-Me), 1.42 (3H, d, *J* = 6.5 Hz, 1-Me); ^{13}C NMR (125 MHz, CDCl_3): δ 47.6 (C-1),

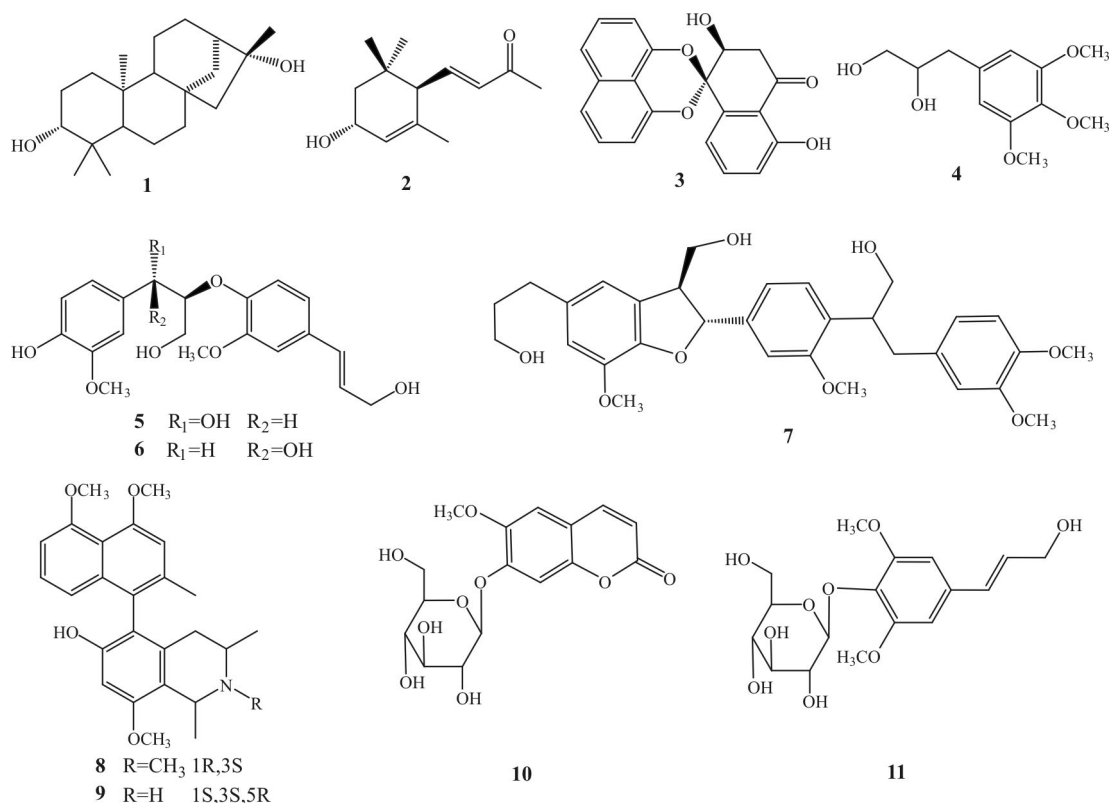


图1 化合物 1~11 的结构

Fig.1 Structures of compounds 1-11

44.4 (C-3), 31.9 (C-4), 116.2 (C-5), 153.8 (C-6), 97.1 (C-7), 156.7 (C-8), 115.0 (C-9), 132.0 (C-10), 120.4 (C-1'), 137.0 (C-2'), 108.4 (C-3'), 157.4 (C-4'), 157.7 (C-5'), 106.6 (C-6'), 128.3 (C-7'), 117.9 (C-8'), 136.8 (C-9'), 116.6 (C-10'), 18.6 (1-Me), 18.8 (3-Me), 20.6 (2'-Me), 55.5 (8-OMe), 56.6 (4'-OMe), 56.4 (5'-OMe)。上述波谱数据与文献[17~18]报道基本一致, 故鉴定此化合物为 hamatine。

东莨菪苷 (Scopolin, 10) 白色固体, mp 220 °C~222 °C; EI-MS m/z : 354 [M]⁺; ¹H NMR (500 MHz, CD₃OD): δ 7.92 (1H, d, J = 9.4 Hz, H-4), 7.23 (1H, s, H-5), 7.19 (1H, s, H-8), 6.32 (1H, d, J = 9.4 Hz, H-3), 5.09 (1H, d, J = 7.4 Hz, H-1'), 3.93 (3H, s, 6-OMe), 4.17~4.53 (6H, m, H-2', H-3', H-4', H-5', H-6'); ¹³C NMR (125 MHz, CD₃OD): δ 162.1 (C-2), 114.5 (C-3), 144.5 (C-4), 110.2 (C-5), 147.2 (C-6), 151.7 (C-7), 104.7 (C-8), 150.7 (C-9), 113.5 (C-10), 101.2 (C-1'), 74.7 (C-2'), 78.4 (C-3'), 71.2 (C-4'), 78.4 (C-5'), 62.5 (C-6'), 57.0 (6-OMe)。上述波谱数据与文献[19]报道基本一致, 故鉴定此化合物为东莨菪苷。

紫丁香苷 (Syringin, 11) 白色固体, mp 189 °C~193 °C; EI-MS m/z : 372 [M]⁺; ¹H NMR (500 MHz, CD₃OD): δ 6.78 (2H, s, H-3, 5), 6.56 (1H, d, J = 15.0 Hz, H-7), 6.37 (1H, m, H-8), 4.14 (2H, m, H-9), 3.88 (6H, 2, 6-OMe), 4.17~4.53 (6H, m, H-2', 3', 4', 5', 6'); ¹³C NMR (125 MHz, CD₃OD): δ 134.2 (C-1), 154.4 (C-2, 6), 104.7 (C-3, 5), 132.2 (C-4), 130.0 (C-7), 129.0 (C-8), 61.6 (C-9), 57.0 (10, 11-OMe), 102.1 (C-1'), 74.3 (C-2'), 77.7 (C-3'), 71.2 (C-4'), 77.3 (C-5'), 61.6 (C-6')。上述波谱数据与文献[20]报道基本一致, 故鉴定此化合物为紫丁香苷。

2 结果和讨论

本文采用多种色谱分离方法, 从黄花三宝木的乙醇提取物中分离得到了 11 个化合物, 通过波谱数据解析及与相关文献对照确定了各化合物的结构, 分别鉴定为: *ent*-kaurane-3β,16β-diol (1)、(3*R*,6*R*,7*E*)-3-hydroxy-4,7-megastigmadien-9-one (2)、palmarumycin JC2 (3)、(±)-3-(3,4,5-trimethoxyphenyl)-1,2-propanediol (4)、赤式-愈创木基甘油-β-*O*-4'-松柏基醚 (5)、苏式-愈创木基甘油-β-*O*-4'

松柏基醚 (6)、3-hydroxymethyl-5-(3-hydroxypropyl)-7-methoxy-2-[3-methoxy-4-[1-(3,4-dimethoxybenzyl)-2-hydroxyethyl]phenyl]-2,3-dihydrobenzofuran (7)、ancistrocline (8)、hamatine (9)、东莨菪苷 (10)、紫丁香苷 (11)。化合物 1 为对映-贝壳杉烷型二萜, 文献报道自然界中主要存在于香茶菜属 (*Isodon*) 植物^[21], 具有抗菌、抗虫^[22]的活性, 由于这类化合物抗肿瘤^[21]活性显著, 现已有针对此类化合物合成研究的报道^[23~24]。化合物 8、9 为萘基四氢异喹啉生物碱, 文献报道此种类型的生物碱具有很好的抗肿瘤^[25]、抗疟、抗 HIV、灭螺^[26]等活性。四氢异喹啉类生物碱中如盐酸小檗碱、延胡索乙素等已经在临床上广泛应用^[27], 而萘基四氢异喹啉生物碱分布于钩枝藤科 (*Ancistrocladaceae*) 植物^[26], 本研究首次从三宝木属植物中分离得到该类化合物, 这与文献报道的三宝木属植物具有抗肿瘤、抗 HIV 活性^[2]相一致。本文丰富了三宝木属植物的化合物类型, 为其资源的开发和利用提供了科学依据。

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