

香花藤化学成分的研究

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摘 要: 目的 对香花藤 *Aganosma marginata* 全株化学成分进行研究。方法 采用硅胶色谱柱、Sephadex LH-20 色谱柱、MCI 色谱柱等方法进行分离纯化, 根据化合物的理化性质和波谱数据鉴定其结构。结果 从香花藤 70%乙醇提取物中分离得到 23 个化合物, 分别鉴定为 periseoside C (1)、3-*O*- β -D-吡喃葡萄糖-3 β ,15 α -二羟基孕甾-5-烯-20-酮 (2)、3 β ,20 α -二羟基-5-烯-孕甾 (3)、24-methylstigmast-5-en-3-ol (4)、29-norcycoloart-23-ene-3,25-diol (5)、29-norcycoloartan-3-ol (6)、京尼平苷酸 (7)、丁香树脂醇 (8)、丁香脂素-4,4'-*O*-双- β -D-吡喃葡萄糖苷 (9)、丁香酸-4-*O*- β -D-葡萄糖苷 (10)、水杨酸 (11)、东莨菪内酯 (12)、壬二酸 (13)、3-*O*-[β -D-xylopyranosyl]-(1 $\rightarrow$ 4)- β -D-allopyranoside-14-hydroxycard-20(22)-enolide (14)、bis (2-ethylhexyl) phthalate (15)、山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)- α -L-吡喃葡萄糖苷 (16)、山柰酚 3-*O*- α -L-吡喃葡萄糖-(1 $\rightarrow$ 2)- β -D-吡喃葡萄糖苷 (17)、山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)-[α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)]- β -D-吡喃葡萄糖苷 (18)、山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)-[β -D-吡喃葡萄糖-(1 $\rightarrow$ 4)]- β -D-吡喃葡萄糖苷 (19)、二十六碳酸-1-甘油酯 (20)、5,8,12-trihydroxy-9-octadecenoic acid (21)、(2*S*,3*S*,4*R*)-phytosphingosine (22)、水粉罩素 (23)。结论 所有化合物均为首次从该属植物中分离得到。

关键词: 香花藤; 京尼平苷酸; 丁香树脂醇; 丁香脂素-4,4'-*O*-双- β -D-吡喃葡萄糖苷; 东莨菪内酯; 山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)- α -L-吡喃葡萄糖苷

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Chemical constituents of *Aganosma marginata*

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Abstract: Objective To investigate the chemical constituents from *Aganosma marginata* and to provide the material basis for the quality control. **Methods** The chemical constituents were separated and purified by silica gel Sephadex LH-20, MCI. Their structures were determined by physicochemical properties and spectral data analyses. **Results** Twenty three compounds were isolated from *A. marginata* and identified as: periseoside C (1), 3-*O*- β -D-glucopyranosyl-3 β ,15 α -dihydroxypregn-5-en-20-one (2), 3 β ,20 α -dihydroxy-5-en-pregnane (3), 28-methylstigmast-5-en-3-ol (4), 29-norcycoloart-23-ene-3,25-diol (5), 29-norcycoloartan-3-ol (6), geniposidic acid (7), syringaresinol (8), syringaresinol-4,4'-*O*-bis- β -D-glucopyranoside (9), syringic acid 4-*O*- β -D-glucopyranoside (10), salicylic acid (11), scopoletin (12), azelaic acid (13), 3-*O*-[β -D-xylopyranosyl]-(1 $\rightarrow$ 4)- β -D-allopyranoside-14-hydroxycard-20 (22)-enolide (14), bis (2-ethylhexyl) phthalate (15), kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- α -L-glucopyranoside (16), kaempferol-3-*O*- α -L-glucopyranoside-(1 $\rightarrow$ 2)- β -D-glucopyranoside (17), kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[α -L-rhamnopyranosyl (1 $\rightarrow$ 4)]- β -D-glucopyranoside (18), kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[β -D-glucopyranosyl-(1 $\rightarrow$ 4)]- β -D-glucopyranoside (19), hexacosanoic acid 1-carbonate (20), 5,8,12-trihydroxy-9-octadecenoic acid (21), (2*S*,3*S*,4*R*)-phytosphingosine (22), and nebularine (23). **Conclusion** All the compounds are obtained from plants of *Aganosma* G. Don for the first time.

Key words: *Aganosma marginata* (Roxb.) G. Don; geniposidic acid; syringaresinol; syringaresinol-4,4'-*O*-bis- β -D-glucopyranoside; scopoletin; 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- α -L-glucopyranoside

夹竹桃科(Apocynaceae)香花藤属 *Aganosma* G. Don 有 15 种, 分布于亚洲热带地区, 该属植物我国

有 5 个种和 3 个变种, 产于南部和西南部。香花藤 *Aganosma marginata* (Roxb.) G. Don 的根、叶味淡、

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平,能利水消肿,用于治疗水肿^[1]。根据细谷孝博对植物提取物(KKP)的筛选,发现香花藤的提取物能干扰 Gli-1 蛋白表达,抑制其转录活性^[2]。根据 Prayong 等^[3]对香花藤细胞活性筛选,发现 50%乙醇香花藤茎提取物对恶性肝癌具有中度细胞毒性和较小的选择性。根据查阅文献,本属植物的研究资料缺乏,仅就其植物分类方面进行一定的研究,而对其化学成分的研究从未见报道,香花藤化学成分的研究可为今后该属植物的研究提供一定的借鉴作用。本实验从香花藤全株 70%乙醇提取物中分离得到 23 个化合物,分别鉴定为 periseoside C (**1**)、3-*O*- β -D-吡喃葡萄糖-3 β ,15 α -二羟基孕甾-5-烯-20-酮(3-*O*- β -D-glucopyranosyl-3 β ,15 α -dihydroxypregn-5-en-20-one, **2**)、3 β ,20 α -二羟基-5-烯-孕甾(3 β ,20 α -dihydroxy-5-en-pregane, **3**)、24-methyl-stigmast-5-en-3-ol(**4**)、29-norcycloart-23-ene-3,25-diol(**5**)、29-norcycloartan-3-ol(**6**)、京尼平苷酸(geniposidic acid, **7**)、丁香树脂醇(syringaresinol, **8**)、丁香脂素-4,4'-*O*-双- β -D-吡喃葡萄糖苷(syringaresinol-4,4'-*O*-bis- β -D-glucopyranoside, **9**)、丁香酸-4-*O*- β -D-葡萄糖苷(syringic acid 4-*O*- β -D-glucopyranoside, **10**)、水杨酸(salicylic acid, **11**)、东莨菪内酯(scopoletin, **12**)、壬二酸(azelaic acid, **13**)、3-*O*-[β -D-xylopyranosyl]-(1 $\rightarrow$ 4)- β -D-allopyranoside-14-hydroxycard-20(22)-enolide(**14**)、bis(2-ethylhexyl) phthalate(**15**)、山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)- α -L-吡喃葡萄糖苷[kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- α -L-glucopyranoside, **16**]、山柰酚 3-*O*- α -L-吡喃葡萄糖-(1 $\rightarrow$ 2)- β -D-吡喃葡萄糖苷(kaempferol-3-*O*- α -L-glucopyranoside-(1 $\rightarrow$ 2)- β -D-glucopyranoside, **17**)、山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)-[α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)]- β -D-吡喃葡萄糖苷(kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]- β -D-glucopyranoside, **18**)、山柰酚 3-*O*- α -L-吡喃鼠李糖-(1 $\rightarrow$ 4)-[β -D-吡喃葡萄糖(1 $\rightarrow$ 4)]- β -D-吡喃葡萄糖苷(kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-[β -D-glucopyranosyl(1 $\rightarrow$ 4)]- β -D-glucopyranoside, **19**)、二十六碳酸-1-甘油酯(hexacosanoic acid 1-carbonate, **20**)、5,8,12-trihydroxy-9-octadecenoic acid(**21**)、(2*S*,3*S*,4*R*)-phytosphingosine(**22**)、水粉覃素(nebularine, **23**)。所有化合物均为首次从香花藤属植物中分离得到并进行结构鉴定。

1 仪器与试剂

XRC-1 微量熔点仪(四川大学科学仪器厂), BrukerAM-400/500 核磁共振光谱仪, BIO-Rad FTS-135 型红外光谱仪, Auto Spec-3000 质谱仪(英国 VG 公司)。柱色谱硅胶(200~300 目)、GF₂₅₄ 和硅胶 G 为青岛海洋化工厂产品, Sephadex LH-20 凝胶(Pharmacia 公司), RP₁₈ gel(Merck 公司), MCI gel CHP-20P(粒径 70~150 μ m, 日本三菱化学公司)。

香花藤采自云南西双版纳,由中国科学院版纳植物所张顺成鉴定为香花藤 *Aganosma marginata* (Roxb.) G. Don 的全株,标本(200601523)保存在中国科学院昆明植物研究所植物化学实验室罗士德研究组。

2 提取与分离

干香花藤全株 5.1 kg,用 70%乙醇热提取 3 次(4、4、3 h),然后分别用石油醚、醋酸乙酯、正丁醇各萃取 3 次(每次 3 L)。醋酸乙酯和正丁醇部分合并后(113 g)经硅胶柱色谱,氯仿-甲醇(1:0~0:1)梯度洗脱,收集到 5 个组分 1~5。组分 2(14 g)过 MCI 柱(甲醇-水 8:2)脱叶绿素后,经正相硅胶柱色谱,氯仿-丙酮(1:0~0:1)洗脱,再经 Sephadex LH-20、RP₁₈、反复硅胶柱色谱处理后得到化合物 **11**(32 mg)、**12**(46 mg)、**20**(21 mg)。组分 3(17 g)过 MCI 柱(甲醇-水 8:2)脱叶绿素后,再分别经正相硅胶柱色谱,氯仿-丙酮(1:0~0:1)洗脱,用 Sephadex LH-20、RP₁₈ 反相柱色谱后,再反复用正相硅胶柱色谱处理后得到化合物 **2**(13 mg)、**3**(45 mg)、**4**(68 mg)、**5**(17 mg)、**6**(28 mg)、**8**(5 mg)、**21**(378 mg)。组分 4(19 g)过 MCI(甲醇-水 8:2)脱色素后,再经正相硅胶(20 g)柱色谱,氯仿-丙酮(1:0~0:1)进行洗脱,然后再用 Sephadex LH-20,反相柱色谱后,再反复用硅胶柱色谱处理后得到化合物 **9**(9 mg)、**10**(10 mg)、**13**(9 mg)、**15**(7 mg)、**22**(21 mg),组分 5(22 g)过 MCI(甲醇-水 0:0~1:0)脱色素和糖后,然后再用 Sephadex LH-20,反相柱色谱后,再反复用硅胶柱色谱处理后得到化合物 **7**(24 mg)、**14**(13 mg)、**16**(39 mg)、**17**(19 mg)、**18**(33 mg)、**19**(27 mg)、**23**(17 mg)。

3 结构鉴定

化合物 **1**:白色粉末,分子式为 C₃₃H₅₄O₁₂, FAB-MS *m/z*: 641 [M-H]⁻(100), 479(11), 391(6),

101 (47)。¹H-NMR (400 MHz, CD₃OD) δ : 1.99 (1H, m, H-1a), 1.35 (1H, m, H-1b), 1.59 (1H, m, H-2a), 1.22 (1H, m, H-2b), 4.26 (1H, m, H-3), 2.61 (1H, d, J = 7.8 Hz, H-4a), 1.34 (1H, m, H-4b), 5.11 (1H, brs, H-6), 2.00 (1H, m, H-7a), 1.65 (1H, m, H-7b), 1.22 (1H, m, H-8), 1.55 (1H, m, H-9), 1.37 (2H, t, J = 11.1 Hz, H-11), 1.61 (1H, m, H-12a), 1.62 (1H, m, H-17), 0.86 (1H, m, H-12b), 1.78 (1H, m, H-14), 1.62 (1H, m, H-15a), 1.09 (1H, m, H-15b), 1.55 (1H, m, H-16a), 1.40 (1H, m, H-16b), 0.85 (3H, s, H-18), 0.63 (3H, s, H-19), 4.27 (2H, overlap, H-5'', 20), 5.01 (1H, d, J = 7.7 Hz, H-1'), 4.29 (1H, m, H-2'), 4.55 (1H, brs, H''-6a), 4.27 (1H, m, H''-6b), 1.17 (3H, d, J = 5.8 Hz, H-21); ¹³C-NMR (100 MHz, CD₃OD) δ : 34.8 (t, C-1), 30.1 (t, C-2), 77.2 (t, C-3), 39.4 (t, C-4), 139.9 (s, C-5), 117.6 (d, C-6), 30.1 (t, C-7), 40.3 (t, C-8), 49.9 (d, C-9), 34.6 (s, C-10), 21.9 (t, C-11), 37.4 (t, C-12), 43.9 (s, C-13), 55.0 (d, C-14), 25.7 (t, C-15), 23.5 (t, C-16), 56.7 (d, C-17), 12.0 (q, C-18), 13.1 (q, C-19), 75.1 (d, C-20), 19.0 (t, C-21), 102.4 (d, C-1'), 75.4 (d, C-2'), 78.8 (d, C-3'), 72.4 (d, C-4'), 78.6 (d, C-5'), 63.5 (t, C-6'), 101.1 (d, C-1''), 75.3 (s, C-2''), 78.7 (d, C-3''), 71.8 (d, C-4''), 78.3 (d, C-5''), 62.9 (t, C-6'')。以上数据与文献报道基本一致^[4], 故鉴定化合物 **1** 为 periseoside C。

化合物 **2**: 无色晶体, 分子式为 C₂₇H₄₂O₈, FAB-MS m/z : 493 [M-H]⁻ (100), 471 (3), 431 (5), 381 (3), 80 (4)。¹H-NMR (400 MHz, CD₃OD) δ : 5.27 (1H, d, J = 2.2 Hz, H-6), 4.38 (1H, d, J = 7.8 Hz, H-1'), 3.63 (2H, m, H-3, 15), 3.63 (4H, m, H-2', 3', 4', 6'), 3.14 (1H, m, H-5'), 2.81 (1H, m, H-17), 0.82 (3H, s, H-19), 0.54 (3H, s, H-18); ¹³C-NMR (100 MHz, CD₃OD) δ : 216.2 (s, C-20), 138.1 (s, C-5), 120.6 (d, C-6), 102.4 (d, C-1'), 79.0 (d, C-3), 78.9 (d, C-3'), 77.9 (d, C-5'), 75.2 (d, C-4'), 71.7 (d, C-2'), 63.7 (d, C-15), 62.9 (t, C-6'), 54.0 (d, C-17), 50.9 (d, C-14), 49.8 (d, C-9), 44.3 (s, C-13), 41.5 (d, C-8), 38.3 (t, C-4), 35.4 (t, C-12), 35.2 (s, C-10), 31.5 (q, C-19), 31.5 (t, C-1), 30.8 (t, C-7), 30.4 (t, C-2), 25.9 (t, C-16), 23.9 (t, C-11), 13.3 (q, C-21), 8.1 (q, C-18)。以上数据与文献报道基本一致^[5], 故鉴定化合物 **2** 为 3-*O*- β -D-吡喃葡萄糖-3 β ,15 α -二羟基孕甾-5-烯-20-酮。

化合物 **3**: 白色粉末, 分子式为 C₂₁H₃₄O₂, EI-MS

m/z : 318 [M]⁺ (100), 300 (31), 282 (36), 267 (53), 246 (28)。¹H-NMR (400 MHz, C₅D₅N) δ : 5.06 (1H, d, J = 3.9 Hz, H-6), 3.84 (1H, m, H-3), 1.30 (3H, d, J = 6.0 Hz, 21-CH₃), 0.78 (3H, s, 18-CH₃), 0.97 (3H, s, 19-CH₃); ¹³C-NMR (100 MHz, C₅D₅N) δ : 138.5 (s, C-5), 115.6 (d, C-6), 75.5 (d, C-3), 69.9 (d, C-20), 58.8 (d, C-17), 54.9 (d, C-14), 44.3 (s, C-13), 40.3 (t, C-4), 36.3 (d, C-9), 36.3 (d, C-8), 34.0 (s, C-10), 33.2 (t, C-12), 30.8 (t, C-1), 28.5 (t, C-7), 27.1 (t, C-2), 25.9 (t, C-16), 25.2 (q, C-19), 24.4 (q, C-21), 23.7 (t, C-15), 22.0 (t, C-11), 12.6 (q, C-18)。以上数据与文献报道基本一致^[6], 故鉴定化合物 **3** 为 3 β ,20 α -二羟基-5-烯-孕甾。

化合物 **4**: 白色粉末, 分子式为 C₃₀H₅₂O, FAB-MS m/z : 427 [M-H]⁻ (100), 381 (7), 393 (22)。¹H-NMR (400 MHz, C₅D₅N) δ : 3.46 (1H, m, H-3), 1.08 (3H, s, H-18), 1.06 (3H, s, H-19), 0.68 (3H, s, H-29), 0.98 (3H, d, J = 6.4 Hz, H-21), 0.88 (3H, d, J = 5.3 Hz, H-27), 0.87 (3H, d, J = 5.3 Hz, H-28); ¹³C-NMR (100 MHz, C₅D₅N) δ : 142.1 (s, C-5), 121.3 (d, C-6), 71.4 (d, C-3), 57.0 (d, C-17), 56.4 (d, C-14), 50.6 (d, C-9), 49.7 (s, C-4), 46.2 (d, C-13), 43.5 (t, C-12), 37.9 (t, C-22), 36.5 (s, C-10), 36.5 (d, C-20), 34.3 (t, C-29), 32.7 (d, C-25), 32.3 (t, C-2), 30.1 (t, C-7), 29.6 (d, C-25), 28.6 (t, C-16), 26.5 (t, C-2), 25.6 (s, C-24), 24.6 (t, C-15), 21.4 (t, C-11), 20.0 (q, C-18), 20.0 (q, C-19), 19.7 (q, C-21), 19.7 (q, C-27), 19.3 (q, C-29), 19.1 (q, C-30), 12.1 (q, C-25)。以上数据与文献报道基本一致^[7], 故鉴定化合物 **4** 为 24-methylstigmast-5-en-3-ol。

化合物 **5**: 白色粉末, 分子式为 C₂₉H₄₈O₂, FAB-MS m/z : 427 [M-H]⁻ (15), 411 (100), 393 (22)。¹H-NMR (400 MHz, C₅D₅N) δ : 5.98 (1H, d, J = 15.6 Hz, H-24), 5.92 (1H, d, J = 15.6 Hz, H-25), 3.46 (1H, m, H-3), 1.54 (3H, s, H-26), 1.03 (3H, s, H-27), 0.99 (3H, s, H-18), 0.88 (3H, s, H-29), 1.25 (3H, d, J = 6.5 Hz, H-21), 0.95 (3H, d, J = 6.2 Hz, H-28); ¹³C-NMR (100 MHz, C₅D₅N) δ : 141.7 (d, C-24), 124.6 (d, C-23), 75.8 (d, C-3), 69.8 (s, C-25), 52.2 (d, C-17), 49.2 (s, C-14), 47.0 (d, C-8), 45.6 (s, C-14), 45.3 (s, C-13), 45.4 (d, C-6), 43.8 (d, C-4), 39.5 (t, C-22), 36.9 (d, C-20), 35.9 (t, C-12), 35.6 (t, C-1), 33.1 (t, C-11), 31.3 (t, C-15), 30.9 (q, C-26), 30.9 (q,

C-27), 30.0 (s, C-10), 28.3 (t, C-2), 27.2 (t, C-7), 25.5 (t, C-6), 25.1 (t, C-16), 23.6 (s, C-9), 19.3 (q, C-21), 18.6 (q, C-29), 18.1 (q, C-28), 15.2 (q, C-18)。以上数据与文献报道基本一致^[8], 故鉴定化合物 **5** 为 29-norcycloart-23-ene-3,25-diol。

化合物 **6**: 白色粉末, 分子式为 $C_{29}H_{50}O$, FAB-MS m/z : 413 $[M-H]^-$ (100), 381 (7), 393 (22)。 1H -NMR (400 MHz, C_5D_5N) δ : 3.46 (1H, m, H-3), 1.54 (3H, s, H-26), 1.52 (1H, s, H-19a), 1.28 (1H, s, H-19b), 1.00 (3H, s, H-27), 0.89 (3H, s, H-29), 1.25 (1H, d, $J = 6.4$ Hz, H-28); ^{13}C -NMR (100 MHz, C_5D_5N) δ : 75.9 (d, C-3), 52.9 (d, C-17), 49.7 (s, C-13), 47.1 (d, C-8), 45.7 (s, C-14), 45.4 (d, C-6), 43.8 (d, C-4), 36.4 (d, C-20), 35.9 (t, C-12), 35.6 (t, C-1), 33.3 (t, C-11), 31.4 (t, C-15), 30.1 (s, C-10), 28.5 (t, C-2), 27.4 (t, C-7), 26.2 (q, C-26), 26.1 (q, C-27), 25.9 (t, C-6), 25.5 (t, C-16), 23.7 (s, C-9), 19.4 (q, C-21), 18.9 (q, C-29), 18.1 (q, C-28), 15.2 (q, C-18)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **6** 为 29-norcycloartan-3-ol。

化合物 **7**: 白色粉末, 分子式为 $C_{16}H_{22}O_{10}$, FAB-MS m/z : 527 (77), 373 $[M-H]^-$ (100), 311 (7)。 1H -NMR (500 MHz, C_5D_5N) δ : 7.95 (1H, s, H-3), 5.98 (1H, s, H-6), 5.72 (1H, d, $J = 7.0$ Hz, H-1'), 5.43 (1H, d, $J = 7.8$ Hz, H-1''), 4.80 (1H, d, $J = 14.6$ Hz, H-6'a), 4.53 (1H, d, $J = 14.7$ Hz, H-6'b), 4.47 (1H, d, $J = 11.8$ Hz, H-10); ^{13}C -NMR (125 MHz, C_5D_5N) δ : 169.7 (s, C-11), 151.9 (d, C-3), 145.6 (s, C-7), 126.8 (d, C-6), 113.0 (s, C-4), 101.2 (d, C-1), 97.9 (d, C-1'), 78.8 (d, C-5'), 78.5 (d, C-3'), 74.8 (d, C-2'), 71.5 (d, C-4'), 62.6 (t, C-6'), 60.9 (t, C-10), 47.2 (d, C-9), 39.3 (t, C-8), 36.1 (d, C-5)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **7** 为京尼平苷酸。

化合物 **8**: 白色晶体 (水), 分子式为 $C_{22}H_{26}O_8$, EI-MS m/z : 419 $[M]^+$ (100), 203 (42), 236 (45), 221 (29), 210 (42), 193 (44), 154 (59); IR ν_{max}^{KBr} (cm^{-1}): 3 441, 3 005, 2 943, 1 612, 1 520, 1 456, 1 426, 1 379, 1 247, 1 204, 1 156, 1 063, 986, 962, 912, 851, 728。 1H -NMR (400 MHz, C_5D_5N) δ : 6.99 (4H, s, H-2, 6, 2', 6'), 4.67 (2H, d, $J = 4.3$ Hz, H-7, 7'), 4.21 (2H, dd, $J = 8.9, 6.8$ Hz, H-9a, 9'a), 3.83 (2H, dd, $J = 9.0, 3.5$ Hz, H-9b, 9'b), 3.78 (12H, s, $4 \times -OCH_3$), 3.05 (2H, m, H-8, 8'); ^{13}C -NMR (100 MHz, C_5D_5N) δ : 153.9 (s,

C-3, 5), 137.4 (s, C-4, 4'), 132.1 (s, C-1, 1'), 104.0 (d, C-2, 2', 6, 6'), 86.1 (d, C-7, 7'), 72.2 (t, C-9, 9'), 56.4 (s, $4 \times -OCH_3$), 54.8 (d, C-8, 8')。以上数据与文献报道基本一致^[11], 故鉴定化合物 **8** 为丁香树脂醇。

化合物 **9**: 白色粉末, 分子式为 $C_{34}H_{46}O_{18}$, FAB-MS m/z : 741 $[M-H]^-$ (60), 637 (17), 185 (43), 137 (55)。 1H -NMR (500 MHz, C_5D_5N) δ : 7.03 (4H, s, H-2, 2', 6, 6'), 5.82 (2H, m, H-1''', 1'''), 4.94 (2H, d, $J = 3.2$ Hz, H-7, 7'), 3.78 (6H, s, $2 \times -OCH_3$), 3.59 (6H, s, $2 \times -OCH_3$); ^{13}C -NMR (125 MHz, C_5D_5N) δ : 154.0 (s, C-3, 5), 138.3 (s, C-4, 4'), 123.1 (s, C-1, 1'), 105.0 (d, C-2, 2', 6, 6'), 104.9 (d, C-1''', 1'''), 86.2 (d, C-7, 7'), 78.7 (d, C-3''', 3'''), 78.4 (d, C-5''', 5'''), 76.1 (d, C-2''', 2'''), 72.3 (t, C-9, 9'), 71.7 (d, C-4''', 4'''), 62.7 (t, C-6''', 6'''), 56.7 (q, $4 \times -OCH_3$), 54.8 (d, C-8, 8')。以上数据与文献报道基本一致^[12], 故鉴定化合物 **9** 为丁香脂素-4,4'-O-双- β -D-葡萄糖苷。

化合物 **10**: 白色粉末, 分子式为 $C_{15}H_{20}O_{10}$, FAB-MS m/z : 359 $[M-H]^-$ (100), 325 (6), 255 (7)。 1H -NMR (500 MHz, D_2O) δ : 7.76 (2H, s, H-2, 6), 5.99 (1H, d, $J = 7.5$ Hz, H-1'), 4.41 (1H, m, H-2'), 4.38 (1H, m, H-6'a), 4.35 (1H, m, H-6'b), 4.33 (1H, m, H-5'), 4.31 (1H, m, H-4'), 4.28 (1H, m, H-3'), 3.76 (3H, s, $-OCH_3$), 3.58 (3H, s, $-OCH_3$); ^{13}C -NMR (125 MHz, D_2O) δ : 167.5 (s, C=O), 153.7 (s, C-3, 5), 137.5 (s, C-4), 128.2 (s, C-1), 109.2 (d, C-2, 6), 104.1 (d, C-1'), 77.8 (d, C-3'), 77.1 (d, C-5'), 75.1 (d, C-2'), 70.8 (d, C-4'), 62.0 (t, C-6'), 57.9 (q, $-OCH_3$)。以上数据与文献报道基本一致^[13], 故鉴定化合物 **10** 为丁香酸-4 β -D-吡喃葡萄糖苷。

化合物 **11**: 白色晶体 (水), 分子式为 $C_7H_6O_3$, FAB-MS m/z : 137 $[M-H]^-$ (100), 119 (5), 82 (10)。 1H -NMR (500 MHz, C_5D_5N) δ : 8.27 (1H, d, $J = 7.8$ Hz, H-6), 7.46 (1H, t, $J = 7.9, 7.4$ Hz, H-4), 7.18 (1H, $J = 8.3$ Hz, H-3), 6.94 (1H, t, $J = 7.5$ Hz, H-5); ^{13}C -NMR (125 MHz, C_5D_5N) δ : 174.8 (s, C-1), 163.0 (s, C-2), 135.3 (d, C-4), 131.5 (d, C-6), 119.2 (d, C-5), 117.7 (d, C-3), 115.9 (s, C-1)。以上数据与文献报道基本一致^[14], 故鉴定化合物 **11** 为水杨酸。

化合物 **12**: 白色晶体 (水), 分子式为 $C_{10}H_8O_4$, FAB-MS m/z : 176 (4), 191 $[M-H]^-$ (100), 283 (34), 307 (39)。 1H -NMR (500 MHz, C_5D_5N) δ : 7.67 (1H, d, $J = 9.4$ Hz, H-4), 7.12 (1H, s, H-5), 7.03 (1H, s, H-8),

6.29 (1H, d, $J = 9.4$ Hz, H-3), 3.75 (3H, s, -OCH₃); ¹³C-NMR (125 MHz, C₅D₅N) δ : 161.5 (s, C-2), 109.5 (d, C-3), 144.1 (d, C-4), 112.4 (d, C-5), 153.1 (s, C-6), 151.2 (s, C-7), 104.2 (d, C-8), 146.3 (s, C-9), 111.1 (s, C-10), 56.3 (q, -OCH₃)。以上数据与文献报道基本一致^[15], 故鉴定化合物 **12** 为东莨菪内酯。

化合物 **13**: 白色粉末, 分子式为 C₉H₁₆O₄, FAB-MS m/z : 187 [M-H]⁻ (100), 169 (5), 127 (9)。¹H-NMR (400 MHz, C₅D₅N) δ : 2.46 (4H, m, H-2, 8), 1.74 (4H, m, H-3, 7), 1.28 (6H, m, H-4, 5, 6); ¹³C-NMR (100 MHz, C₅D₅N) δ : 176.1 (s, C-1, 9), 34.9 (t, C-2, 8), 29.5 (t, C-4, 5, 6), 25.7 (t, C-3, 7)。以上数据与文献报道基本一致^[16], 故鉴定化合物 **13** 为壬二酸。

化合物 **14**: 白色粉末, 分子式为 C₃₅H₅₄O₁₂, FAB-MS m/z : 665 [M-H]⁻ (21), 635 (5), 391 (39), 339 (4), 277 (100)。¹H-NMR (400 MHz, C₅D₅N) δ : 6.12 (1H, s, H-21), 5.13 (1H, d, $J = 7.5$ Hz, H-1'), 4.95 (1H, d, $J = 7.5$ Hz, H-1''), 4.50 (1H, m, H-3'), 4.27 (1H, d, $J = 6.1$ Hz, H-3), 4.24 (2H, overlap, H-23), 4.10 (2H, overlap, H-4', 3''), 4.00 (4H, overlap, H-2', 5', 2'', 5''), 3.59 (3H, s, -OCH₃), 0.99 (3H, d, $J = 3.4$ Hz, H-6'), 0.72 (3H, s, H-19); ¹³C-NMR (100 MHz, C₅D₅N) δ : 176.0 (s, C-23), 174.7 (s, C-20), 117.8 (d, C-22), 105.4 (d, C-1'), 105.2 (d, C-1''), 84.7 (s, C-14), 83.0 (d, C-4'), 82.9 (d, C-3), 79.5 (d, C-3''), 78.3 (d, C-3'), 75.4 (d, C-5''), 75.2 (t, C-21), 73.9 (d, C-2'), 71.8 (d, C-2''), 63.1 (t, C-5'), 57.5 (q, -OCH₃), 51.5 (d, C-17), 50.1 (s, C-13), 50.1 (d, C-5), 44.5 (d, C-9), 41.8 (d, C-8), 39.8 (t, C-4), 36.2 (t, C-1), 33.2 (t, C-2), 30.1 (t, C-12), 29.3 (t, C-7), 28.1 (t, C-15), 27.4 (t, C-16), 21.7 (t, C-11), 19.0 (q, C-19), 16.3 (q, C-6'), 12.4 (q, C-18)。以上数据与文献报道基本一致^[17], 故鉴定化合物 **14** 为 3-*O*-[β -*D*-xylopyranosyl]-(1 $\rightarrow$ 4)- β -*D*-allopyranoside-14-hydroxycard-20(22)-enolide。

化合物 **15**: 白色粉末, 分子式为 C₂₄H₃₈O₄, FAB-MS m/z : 389 [M-H]⁻ (100), 375 (5), 277 (44)。¹H-NMR (400 MHz, C₅D₅N) δ : 7.90 (2H, d, $J = 6.4$ Hz, H-3, 6), 7.55 (2H, d, $J = 6.4$ Hz, H-4, 5), 4.38 (4H, m, overlap, H-1', 1''), 0.89 (3H, d, $J = 7.5$ Hz, H-6'), 0.84 (3H, d, $J = 6.8$ Hz, H-5''); ¹³C-NMR (100 MHz, C₅D₅N) δ : 168.1 (s, C-1, 8), 131.7 (d, C-3, 6), 129.5 (d, C-4, 5), 68.3 (t, C-1', 1''), 39.2 (t, C-3'), 30.8 (t,

C-4'), 30.1 (t, C-5'), 29.7 (t, C-3''), 24.2 (t, C-4''), 14.4 (q, C-6'), 11.3 (q, C-5'')。以上数据与文献报道基本一致^[18], 故鉴定化合物 **15** 为 bis (2-ethylhexyl) phthalate。

化合物 **16**: 黄色粉末, 分子式为 C₂₇H₃₀O₁₅, FAB-MS m/z : 593 [M-H]⁻ (80), 478 (2), 80 (3)。¹H-NMR (500 MHz, C₅D₅N) δ : 8.42 (2H, d, $J = 8.7$ Hz, H-2', 6'), 7.23 (2H, d, $J = 8.7$ Hz, H-3', 5'), 6.92 (1H, brs, H-8), 6.75 (1H, brs, H-6), 4.65 (1H, d, $J = 2.9$ Hz, H-1''), 4.63 (1H, d, $J = 2.9$ Hz, H-1'''), 1.63 (3H, d, $J = 5.6$ Hz, H-6'''); ¹³C-NMR (125 MHz, C₅D₅N) δ : 178.9 (s, C-4), 162.8 (s, C-7), 162.3 (s, C-5), 161.9 (s, C-4'), 157.8 (s, C-2), 156.9 (s, C-9), 132.0 (s, C-3), 121.9 (s, C-1'), 123.8 (d, C-3', 5'), 116.2 (d, C-2', 6'), 106.9 (s, C-10), 103.7 (d, C-6), 100.4 (d, C-1''), 100.0 (d, C-1'''), 94.9 (d, C-8), 79.2 (d, C-3''), 78.5 (d, C-5''), 76.1 (d, C-2''), 73.6 (d, C-4''), 72.4 (d, C-2'''), 71.6 (d, C-3'''), 71.5 (d, C-5'''), 62.6 (t, C-6''), 18.7 (q, C-6''')。以上数据与文献报道基本一致^[19], 故鉴定化合物 **16** 为山柰酚 3-*O*- α -吡喃鼠李糖-(1 $\rightarrow$ 4)- α -*L*-吡喃葡萄糖苷。

化合物 **17**: 黄色粉末, 分子式为 C₂₇H₃₀O₁₆, FAB-MS m/z : 609 [M-H]⁻ (100)。¹H-NMR (400 MHz, C₅D₅N) δ : 8.42 (2H, d, $J = 8.7$ Hz, H-2', 6'), 7.35 (2H, d, $J = 8.7$ Hz, H-3', 5'), 6.69 (1H, d, $J = 2.0$ Hz, H-8), 6.63 (1H, d, $J = 2.0$ Hz, H-6), 5.61 (1H, d, $J = 7.7$ Hz, H-1''), 5.47 (1H, brs, H-1'''), 4.39~4.17 (9H, m, overlap, H-2''~6''a, 2'''~6'''), 3.97 (1H, d, $J = 2.7$ Hz, H-6''b); ¹³C-NMR (100 MHz, C₅D₅N) δ : 178.9 (s, C-4), 165.7 (s, C-7), 163.0 (s, C-5), 161.7 (s, C-4'), 157.4 (s, C-2), 156.5 (s, C-9), 134.5 (s, C-3), 132.0 (d, C-2', 6'), 122.2 (s, C-1'), 116.3 (d, C-3', 5'), 106.2 (d, C-1''), 105.3 (s, C-10), 100.0 (d, C-1'''), 99.8 (d, C-6), 94.5 (d, C-8), 84.2 (d, C-2''), 79.0 (d, C-3'''), 78.8 (d, C-3''), 78.5 (d, C-5'''), 78.5 (d, C-5''), 76.2 (d, C-2'''), 71.4 (d, C-4''), 71.2 (d, C-4'''), 62.6 (t, C-6''), 62.3 (t, C-6''')。以上数据与文献报道基本一致^[20], 故鉴定化合物 **17** 为山柰酚 3-*O*- α -*L*-吡喃葡萄糖-(1 $\rightarrow$ 2)- β -*D*-吡喃葡萄糖苷。

化合物 **18**: 黄色粉末, 分子式为 C₃₃H₄₀O₁₉, FAB-MS m/z : 739 [M-H]⁻ (100)。¹H-NMR (400 MHz, C₅D₅N) δ : 8.46 (2H, d, $J = 8.7$ Hz, H-2', 6'), 7.32 (2H, d, $J = 8.7$ Hz, H-3', 5'), 6.84 (1H, brs, H-8),

6.72 (1H, brs, H-6), 5.62 (1H, d, $J = 7.5$ Hz, H-1''), 5.05 (1H, d, $J = 1.7$ Hz, H-1'''), 5.03 (1H, d, $J = 1.9$ Hz, H-1'''), 1.64 (1H, d, $J = 5.6$ Hz, H-5''), 1.63 (1H, d, $J = 5.6$ Hz, H-5'''); ^{13}C -NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 178.9 (s, C-4), 165.6 (s, C-7), 162.2 (s, C-5), 161.5 (s, C-4'), 156.8 (s, C-2), 156.5 (s, C-9), 134.4 (s, C-3), 132.1 (d, C-2', 6'), 121.2 (s, C-1'), 116.5 (d, C-3', 5'), 104.3 (s, C-1''), 104.2 (d, C-1'''), 103.8 (d, C-1'''), 99.8 (d, C-8), 94.8 (d, C-6), 78.5 (d, C-3''), 75.8 (d, C-5''), 73.6 (d, C-4''), 72.3 (d, C-4'''), 71.9 (d, C-4'''), 71.7 (d, C-2''), 70.9 (d, C-3'''), 70.8 (d, C-3'''), 70.5 (d, C-2'''), 70.1 (d, C-5'''), 69.5 (d, C-5'''), 69.3 (d, C-5'''), 62.6 (t, C-6''), 17.9 (q, C-6'''), 17.5 (q, C-6'''). 以上数据与文献报道基本一致^[21], 故鉴定化合物 **18** 为山柰酚 3-*O*- α -*L*-吡喃鼠李糖-(1 $\rightarrow$ 4)-[α -*L*-吡喃鼠李糖-(1 $\rightarrow$ 4)]- β -*D*-吡喃葡萄糖苷。

化合物 **19**: 黄色粉末, 分子式为 $\text{C}_{33}\text{H}_{40}\text{O}_{20}$, FAB-MS m/z : 755 $[\text{M}-\text{H}]^-$ (5), 701 (3), 609 (100), 447 (7), 285 (54), 127 (7)。 ^1H -NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 8.47 (2H, d, $J = 8.7$ Hz, H-2', 6'), 7.39 (2H, d, $J = 8.7$ Hz, H-3', 5'), 6.84 (1H, brs, H-8), 6.72 (1H, brs, H-6), 5.62 (1H, d, $J = 7.5$ Hz, H-1''), 4.70 (1H, brs, H-1'''), 4.64 (1H, d, $J = 7.5$ Hz, H-1'''), 1.63 (3H, d, $J = 5.6$ Hz, H-6'''); ^{13}C -NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 179.0 (s, C-4), 162.6 (s, C-7), 162.4 (s, C-5), 161.9 (s, C-4'), 156.8 (s, C-2), 156.7 (s, C-9), 134.6 (s, C-3), 132.2 (d, C-2', 6'), 121.9 (s, C-1'), 116.4 (d, C-3', 5'), 106.9 (s, C-10), 106.3 (d, C-1''), 100.4 (d, C-1'''), 100.0 (d, C-1'''), 99.8 (d, C-6), 94.7 (d, C-8), 84.3 (d, C-2''), 79.23 (d, C-3''), 78.8 (d, C-3'''), 78.6 (d, C-5''), 78.5 (d, C-5'''), 76.2 (d, C-2'''), 73.6 (d, C-4''), 72.4 (d, C-4'''), 71.7 (d, C-4'''), 71.5 (d, C-2''), 71.3 (d, C-3'''), 71.1 (d, C-5'''), 62.5 (t, C-6''), 62.2 (t, C-6'''), 18.7 (q, C-6'''). 以上数据与文献报道基本一致^[22], 故鉴定化合物 **19** 为山柰酚 3-*O*- α -*L*-吡喃鼠李糖-(1 $\rightarrow$ 4)-[β -*D*-吡喃葡萄糖 (1 $\rightarrow$ 4)]- β -*D*-吡喃葡萄糖苷。

化合物 **20**: 无色蜡状物, 分子式为 $\text{C}_{29}\text{H}_{58}\text{O}_4$, EI-MS m/z : 470 $[\text{M}]^+$ (1)。 ^1H -NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 4.71 (1H, m, H-1a), 4.64 (1H, m, H-1b), 4.44 (1H, t, $J = 5.4, 5.2$ Hz, H-2), 4.12 (2H, d, $J = 5.4$ Hz, H-3), 2.34 (2H, t, $J = 7.5, 7.4$ Hz, H-2'), 0.86 (3H, m, H-25'); ^{13}C -NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 174.3 (s, C-1'), 69.6 (d, C-2), 66.7 (t, C-1), 63.4 (t, C-3), 33.8 (t,

C-2'), 29.4~28.8 (t, C-4'~22'), 24.5 (t, C-3'), 22.3 (t, C-24'), 31.6 (t, C-25'), 13.6 (q, C-26')。以上数据与文献报道基本一致^[23], 故鉴定化合物 **20** 为二十六碳酸-1-甘油酯。

化合物 **21**: 白色粉末, 分子式为 $\text{C}_{18}\text{H}_{34}\text{O}_5$, FAB-MS m/z : 329 $[\text{M}-\text{H}]^-$ (100), 315 (12), 301 (4)。 ^1H -NMR (500 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 5.57 (1H, m, H-9), 5.56 (1H, m, H-10), 3.33 (1H, m, H-5), 0.88 (3H, s, H-18); ^{13}C -NMR (125 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 176.9 (s, C-1), 135.6 (d, C-9), 129.5 (d, C-10), 75.2 (d, C-8), 74.6 (d, C-12), 71.7 (d, C-5), 36.7 (t, C-2), 34.0 (t, C-11), 31.8 (t, C-7), 29.2 (t, C-6), 28.9 (t, C-3), 28.8 (t, C-4), 25.3 (t, C-13), 25.1 (t, C-14), 24.7 (t, C-15), 24.7 (t, C-16), 22.5 (t, C-17), 13.9 (q, C-18), 以上数据与文献报道基本一致^[24], 故鉴定化合物 **21** 为 5,8,12-trihydroxy-9-octadecenoic acid。

化合物 **22**: 白色粉末, 分子式为 $\text{C}_{44}\text{H}_{83}\text{NO}_9$, IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3 375, 2 923, 1 629, 1 538, 1 465, 1 076, 721; FAB-MS m/z : 787 $[\text{M}-\text{H}-\text{H}_2\text{O}]^-$ (100), 625 (30), 653 (20)。 ^1H -NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 8.37 (1H, d, $J = 8.8$ Hz, NH), 5.97 (2H, m, H-4, 5), 5.48 (2H, m, H-8, 9), 4.91 (1H, d, $J = 4.6$ Hz, H-1''), 0.85 (3H, m, H-18), 0.87 (3H, m, H-20'); ^{13}C -NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 175.7 (s, C-1'), 132.1 (d, C-4), 132.1 (d, C-5), 131.1 (d, C-8), 130.0 (d, C-9), 105.7 (d, C-1''), 78.6 (d, C-3), 78.5 (d, C-2'), 75.2 (d, C-3''), 72.5 (d, C-5''), 72.3 (d, C-2''), 71.5 (d, C-4''), 70.2 (t, C-1), 62.7 (t, C-6''), 54.6 (d, C-2), 35.7 (t, C-6), 33.0 (t, C-7), 32.9 (t, C-10), 32.1 (t, C-3'), 30.1 (t, C-4'), 30.0 (t, C-11), 29.9 (t, C-12), 29.7 (t, C-13), 29.6 (t, C-14), 26.0 (t, C-16), 23.0 (t, C-17), 14.3 (q, C-18)。以上数据与文献报道基本一致^[25], 故鉴定化合物 **22** 为 (2*S*,3*S*,4*R*)-phytosphingosine。

化合物 **23**: 白色粉末, 分子式为 $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_4$, mp 182~183 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} -46.8^{\circ}$ (c 2.0, H_2O); FAB-MS m/z : 251 $[\text{M}-\text{H}]^-$ (81), 235 (5), 190 (19), 98 (17)。 ^1H -NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 8.73 (1H, brs, H-8), 8.71 (1H, brs, H-6), 8.60 (1H, brs, H-2), 6.72 (1H, d, $J = 5.8$ Hz, H-1'), 5.47 (1H, m, H-2'), 5.06 (1H, m, H-3'), 4.76 (1H, m, H-4'), 4.29 (1H, dd, $J = 12.4, 2.5$ Hz, H-5'a), 4.23 (1H, dd, $J = 12.4, 2.5$ Hz, H-5'b); ^{13}C -NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 157.7 (s, C-4), 153.3 (d, C-2), 149.9 (d, C-8), 140.6 (d, C-6), 121.5 (s, C-5),

90.8 (d, C-1'), 87.8 (d, C-4'), 75.6 (d, C-2'), 72.4 (d, C-3'), 63.1 (t, C-5')。以上数据与文献报道基本一致^[26], 故鉴定化合物 **23** 为水粉覃素。

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