金钟藤中酚类化合物的研究

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摘要:从金钟藤 (Merremia boisiana (Gagnep.) V. Ooststr.)的地上部分分离得到 8 个酚类化合物。通过光谱分析,分别鉴定为东莨菪内酯 (1)、七叶内酯 (2)、N-p- 香豆酰酪胺 (3)、3, 5- 二咖啡酰基奎尼酸甲酯 (4)、3, 4- 二咖啡酰基奎尼酸甲酯 (5)、3, 4, 5- 三咖啡酰基奎尼酸甲酯 (6)、槲皮素 (7)以及山奈酚 -3-β-D- 半乳糖甙 (8)。这些化合物均是首次从鱼黄草属(Merremia)植物中发现。

关键词: 金钟藤; 旋花科; 鱼黄草属; 酚类化合物; 化学成分; 化感物质

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Phenolic Compounds from Merremia boisiana (Convolvulaceae)

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Abstract: Eight phenolic compounds were isolated from the aerial parts of *Merremia boisiana* (Convolvulaceae). On the basis of the spectral data, they were identified as scopoletin (1), esculetin (2), paprazine (3), 3,5-di-O-caffeoylquinic acid methyl ester (4), 3,4-di-O-caffeoylquinic acid methyl ester (5), 3,4,5-tri-O-caffeoylquinic acid methyl ester (6), quercetin (7), and kaempferol 3-β-D-galactopyranoside (8). They were all obtained from *Merremia* plants for the first time.

Key words: Merremia boisiana; Convolvulaceae; Merremia; Phenolic compounds; Chemical constituents; Allelochemicals

金钟藤(Merremia boisiana (Gagnep.) V. Ooststr.) 又名多花山猪菜,是旋花科 (Convolvulaceae) 鱼黄草属 (Merremia) 的多年生缠绕大藤本,原分布于广西、云南,越南、老挝等地门。最近发现该植物在广东省广州市附近呈大面积分布四,已成为当地的一个生态有害种。它生长迅速,且多分枝,能缠绕并覆盖其它乔、灌木,致使后者死亡,破坏性极大,严重地影响着分布区物种多样性的丰富度,也危害了当地的农、林业生产[34]。根据入侵生物学理论,外来入侵植物多具有较强化感作用,化感物质是其入侵的新式武器[5]。虽然对鱼黄草属植物的化学成分已有诸

多研究[67],但金钟藤的化学成分未见报道。为了明确金钟藤是否能产生化感物质,揭示其入侵的化学机制,我们对其化学成分进行了研究。本文报道其酚类成分并探讨其酚类成分的生态学意义,为入侵植物金钟藤的防治提供科学依据。

1 材料和方法

1.1 材料

金钟藤(Merremia boisiana (Gagnep.) V. Ooststr.) 于 2004 年 12 月采自广东省龙眼洞林场簸萁窝。柱 层析用硅胶为青岛海洋化工厂生产,柱层析用凝胶

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为 Sephadex LH-20,柱层析用聚酰胺粉和聚酰胺薄层层析板均为浙江省台州市路桥四甲生化塑料厂生产,正相薄层层析板是烟台黄务硅胶开发试验厂生产。

1.2 仪器

核磁共振谱用 Bruker DRX-400 核磁共振仪, 以四甲基硅烷 (TMS) 为内标测定。ESIMS 用 MDS SCIEX API 2000 LC/MS/MS 仪,以甲醇为溶剂,直 接进样测定。比旋光度用 Perkin Elmer 341 旋光仪 测定。紫外光谱用 Perkin Elmer Lambda 25 紫外分 光光度计测定。

1.3 提取和分离

金钟藤干粉(3.8 kg)用 88%的乙醇渗漉提取 6 d。乙醇提取液减压浓缩后加水成悬浮液,依次用 石油醚、氯仿、乙酸乙酯和正丁醇萃取,得到5部分 提取物。氯仿部分提取物(88g)经硅胶柱层析,氯 仿:甲醇(100:0-80:20)梯度洗脱,从氯仿:甲醇 (98:2) 的洗脱部分中用甲醇重结晶得到化合物 1 (60 mg)。乙酸乙酯部分提取物(41 g)经硅胶柱层 析, 氯仿: 甲醇 (99:1-2:1) 梯度洗脱, 得到 F1、F2、 F3、F4 部分。F1 部分再经硅胶柱层析,石油醚:丙酮 (3:1-3:2) 洗脱,从 3:1 洗脱部分用凝胶柱(甲醇洗 脱) 得到化合物 2 (20 mg), 3:2 洗脱部分甲醇重结 晶得到化合物 3 (400 mg)。从 F3 通过聚酰胺柱层析 氯仿:甲醇(9:1-5:1)洗脱后得到3个化合物,分别 用凝胶柱层析(甲醇洗脱)纯化得到化合物 4 (240 mg)、5 (300 mg)和 6 (60 mg)。从 F4 通过聚酰胺 柱层析氯仿:甲醇(6:1-8:1)洗脱后,通过凝胶柱层 析(甲醇洗脱)纯化得到化合物 7 (75 mg)和 8 (15 mg)

1.4 结构鉴定

化合物 1 浅黄色粉末,分子式 $C_{10}H_8O_4$, UV (MeOH) λ_{max} nm (loge): 223 (2.69), 258 (2.35), 295 (2.25), 349 (2.45); 正离子 ESIMS m/z: 193.2 [M + H]⁺, 149 [M - CO₂ + H]⁺; ¹H NMR (400 MHz, CDCl₃): 87.58 (1H, d, J = 9.2 Hz, H-4), 6.90 (1H, s, H-8), 6.83 (1H, s, H-5), 6.25 (1H, d, J = 9.2 Hz, H-3), 6.15 (1H, s, 7-OH), 3.93 (3H, s, OCH₃); ¹³C NMR (100 MHz, CDCl₃): 8161.5 (C-2), 150.2 (C-7), 149.7 (C-9), 144.0 (C-6), 143.3 (C-4), 113.4 (C-3), 111.5 (C-10), 107.5

(C-5), 103.2 (C-8), 56.4 (OCH₃)。光谱数据与文献[8] 报道的东莨菪内酯(scopoletin)一致。

化合物 2 浅黄色粉末,分子式 $C_9H_6O_4$, UV (MeOH) λ_{max} nm (log ϵ): 228 (2.74), 256 (2.66), 300 (2.64), 348 (2.83); 正离子 ESIMS m/z: 179 [M + H]⁺, 196 [M + H₂O]⁺, 201 [M + Na]⁺; ¹H NMR (400 MHz, acetone- d_6): δ 7.76 (1H, d, J= 9.6 Hz, H-4), 7.02 (1H, s, H-5), 6.78 (1H, s, H-8), 6.13 (1H, d, J= 9.6 Hz, H-3)。根据以上数据对照文献[9],确定该化合物是七叶内酯(esculetin)。

化合物3 白色粉末状固体,分子式为 $C_{17}H_{17}NO_3$, UV (MeOH) λ_{max} nm (loge): 205 (2.95), 230 (3.01), 293 (2.99), 305 (3.00); 正离子 ESIMS m/z: 284 [M + H]⁺, 306 [M + Na]⁺; ¹H NMR (400 MHz, acetone- d_6): δ 7.46 (1H, d, J = 16.0 Hz, H-8'), 7.39 (2H, d, J = 8.4 Hz, H-2', H-6'), 7.04 (2H, d, J = 8.4 Hz, H-3', H-5'), 6.82 (2H, d, J = 8.4 Hz, H-3, H-5), 6.73 (2H, d, J = 8.4 Hz, H-2, H-6), 6.46 (1H, d, J=16.0 Hz, H-7'), 3.45 (2H, m, J=7.6 Hz, H-8), 2.72 (2H, t, J = 7.6 Hz, H-7); ¹³C NMR (100 MHz, acetone- d_6): $\delta 166.8$ (C=O), 159.8 (C-4'), 156.6 (C-4), 140.3 (C-8'), 130.9 (C-1'), 130.4 (C-3', C-5'), 130.1 (C-3, C-5), 127.5 (C-1), 119.3 (C-7'), 116.4 (C-2', C-6'), 115.9 (C-2, C-6), 41.8 (C-8), 35.6 (C-7); ¹H NMR 和 ¹³C NMR 数据与文献[10]对照,确定该化合 物是 N-p- 香豆酰酪胺(paprazine)。

化合物 4 黄色无定型粉末,分子式为 $C_{26}H_{26}O_{12}$, [α]_D²⁰ -15.9 (c 0.90, MeOH); 正离子 ESIMS m/z: 531 [M + H] $^+$, 553 [M + Na] $^+$. 1 H NMR (400 MHz, acetone- d_6): $\delta 7.56 \cdot 7.52$ (各 1H, d, J =16.0 Hz, H-7', H-7"), $7.16\sqrt{7.15}$ (各 1H, d, J = 2.0 Hz, H-2', H-2"), $7.01 \cdot 6.99$ (各 1H, dd, J = 2.0 Hz, 8.0 Hz, H-6', H-6"), $6.85 \cdot 6.84$ (各 1H, d, J = 8.0 Hz, H-5', H-5"), 6.29, 6.21 (各 1H, d, J = 16.0 Hz, H-8', H-8"), 5.38 (1H, m, H-5), 5.30 (1H, m, H-3), 4.02 (1H, m, H-4), 3.64 (3H, s, OCH₃), 2.19-2.29 (4H, m, H₂-2, H_2 -6); ¹³C NMR (100 MHz, acetone- d_6): δ 174.9 (C=O), 167.1,166.7 (C-9', C-9"), 149.0,148.8 (C-4', C-4"), 146.3、145.8 (C-3', C-3", C-7', C-7"), 127.4、 127.2 (C-1', C-1") , 122.6、122.4 (C-6', C-6"), 116.3、 116.2 (C-5', C-5"), 115.7,115.4 (C-2', C-2"), 115.0, 114.8 (C-8', C-8"), 74.0 (C-1), 71.8 (C-3), 71.3 (C-4), 69.0 (C-5), 52.6 (OCH₃), 36.5 (C-6), 35.4 (C-2)。对照 文献[11-12]报道数据,确定该化合物为 3, 5-二咖啡 酰基奎尼酸甲酯(3,5-di-*O*-caffeoylquinic acid methyl ester)。

化合物 5 黄色无定型粉末,分子式为 $C_{26}H_{26}O_{12}$, [α] $_{D}^{20}$ -20 (c 0.35, MeOH); 正离子 ESIMS m/z: 531 [M + H] $^{+}$, 553 [M + Na] $^{+}$ 。 'H NMR (400 MHz, CD $_{3}$ OD): δ 7.59、7.50 (各 1H, d, J = 16.0 Hz, H-7', H-7"), 7.06、7.01 (各 1H, d, J = 2.0 Hz, H-2', H-2"), 6.90、6.91 (各 1H, dd, J = 2.0 Hz, 8.0 Hz, H-6', H-6''), 6.78、6.75 (各 1H, d, J = 8.0 Hz, H-5', H-5"), 6.29、6.16 (各 1H, d, J = 16.0 Hz, H-8', H-8"), 5.54 (1H, m, H-3), 5.11 (1H, m, H-4), 4.34 (1H, m, H-5), 3.70 (3H, s, OCH $_{3}$), 2.30 -2.21 (4H, m, H $_{2}$ -2, H $_{2}$ -6); 该数据与文献[11-12]对照,确定该化合物为 3,4- 二咖啡酰基奎尼酸甲酯(3,4-di-O-caffeoylquinic acid methyl ester)。

化合物 6 黄色无定型粉末,分子式为 $C_{35}H_{32}O_{15}$, [α] $_{D}^{20}$ -14.45 (c 0.20, MeOH); 负离子 ESIMS m/z: 691 [M-H] $^{-}$ 。 'H NMR (400 MHz, CD₃OD): δ 7.58、7.53、7.53 (各 1H, d, J = 16.0 Hz, H-7', H-7", H-7"), 7.05、7.02、7.00 (各 1H, d, J = 2.0 Hz, H-2', H-2"), 6.94、6.92、6.88 (各 1H, dd,

6 $R_1 = R_2 = caffeoyl$

 $J = 2.0 \text{ Hz}, 8.0 \text{ Hz}, \text{H-6'}, \text{H-6''}, \text{H-6'''}), 6.76 \cdot 6.76 \cdot 6.71$ (各1H, d, J = 8.0 Hz, H-5', H-5", H-5"), $6.29 \times 6.23 \times$ 6.19 (各 1H, d, J = 16.0 Hz, H-8', H-8", H-8"), 5.64 (1H, m, H-5), 5.58 (1H, m, H-3), 5.33 (1H, m, H-4), 3.73 (3H, s, OCH₃), 2.42–2.23 (4H, m, H₂-2, H₂-6); ¹³C NMR (100 MHz, CD₃OD): δ175.5 (C=O), 168.4. 168.0、167.8 (C-9', C-9", C-9""), 149.8、149.8、149.7 (C-4', C-4", C-4""), 148.0 \, 147.9 \, 147.6 (C-7', C-7", C-7"), 147.9, 147.6, 146.8 (C-3', C-3", C-3"), 127.8, 127.6、127.6 (C-1', C-1", C-1""), 123.4、123.2、123.2 (C-6', C-6", C-6"'), 116.5,116.5,116.5 (C-5', C-5", C-5"), 115.2, 115.0, 115.0 (C-2', C-2", C-2"), 114.4, 114.4、114.3 (C-8', C-8", C-8""), 74.7 (C-1), 74.7 (C-4), 69.6 (C-3), 69.3 (C-5), 53.2 (OCH₃), 38.0 (C-6), 36.5 (C-2), 与文献[13]对照, 确定该化合物为 3, 4, 5- 三咖啡酰基奎尼酸甲酯(3, 4, 5-tri-O-caffeoylquinic acid methyl ester).

化合物 7 黄色粉末状固体,分子式为 $C_{15}H_{10}O_7$, $[\alpha]_D^{20}$ –12.96 (c 0.125, MeOH); UV (MeOH) λ_{max} nm (log ε): 257 (3.06), 305 (2.83), 375 (2.83); 负离子 ESIMS m/z: 300.7 [M – H]⁻, 336.9 [M + Cl – H]⁻; 'H NMR (400 MHz, acetone- d_ε): δ 12.15 (1H, s, 5-OH), 7.82 (1H, d, J = 2.0 Hz, H-2'), 7.69 (1H, dd, J =

RO
HO
HO

1 R = CH₃
2 R = H

3

OCH₃
HO
$$\frac{1}{1}$$
 $\frac{1}{1}$
 $\frac{1}{1}$

8.8 Hz, 2.0 Hz, H-6'), 6.98 (1H, d, J = 8.8 Hz, H-5'), 6.51 (1H, d, J = 1.6 Hz, H-8), 6.25 (1H, d, J = 1.6 Hz, H-6), 该化合物 UV 数据与 'H NMR 数据分别对照文献[9,14],确定该化合物为槲皮素(quercetin)。

黄色粉末状固体,分子式为 化合物 8 $C_{21}H_{20}O_{11}$, [α] $_{0}^{20}$ -35 (c 0.10, MeOH); 负离子 ESIMS m/z: 446.9 $[M - H]^-$, 482.4 $[M + Cl - H]^-$; UV (MeOH) λ_{max} nm (log ϵ): 267 (3.12), 300 sh (2.90), 355 (2.92); ¹H NMR (400 MHz, DMSO- d_6): δ 12.61 (1H, s, 5-OH), 8.06 (1H, d, J = 8.8 Hz, H-2'), 8.06 (1H, d, J =8.8 Hz, H-6'), 6.84 (1H, d, J = 8.8 Hz, H-5'), 6.84 (1H, d, J = 8.8 Hz, H-3'), 6.42 (1H, d, J = 2.0 Hz, H-8), 6.20 (1H, d, J = 2.0 Hz, H-6), 5.39 (1H, d, J = 7.6 Hz, H-1"), 3.64 - 5.15 (6H, m, H-2" -6"); ¹³C NMR (100 MHz, DMSO- d_6): δ 177.5 (C-4), 164.1 (C-7), 161.2 (C-5), 159.9 (C-4'), 156.3 (C-2, 9), 133.2 (C-3), 131.0 (C-2', 6'), 120.8 (C-1'), 115.0 (C-3', 5'), 103.9 (C-10), 101.7 (C-1"), 98.7 (C-6), 93.6 (C-8), 75.8 (C-5"), 73.1 (C-3"), 71.2 (C-2"), 67.9 (C-4"), 60.2 (C-6"), 光谱数据与文献[15-16]对照, 确定化合物为 山奈酚 -3-β-D- 半乳糖甙(kaempferol 3-β-D-galactopyranoside).

2 结果和讨论

本研究从金钟藤地上部分分离得到 8 个酚类化合物,通过光谱分析鉴定了它们的结构,其中有两个香豆素类化合物: 东莨菪内酯 (scopoletin, 1)和七叶内酯 (esculetin, 2),一个酰胺化合物 N-p- 香豆酰酪胺 (paprazine, 3),三个咖啡酰基奎尼酸甲酯: 3,5-二咖啡酰基奎尼酸甲酯 (3,5-di-O-caffeoylquinic acid methyl ester, 4)、3,4-二咖啡酰基奎尼酸甲酯(3,4-di-O-caffeoylquinic acid methyl ester, 5)和 3,4,5-三咖啡酰基奎尼酸甲酯 (3,4,5-tri-O-caffeoylquinic acid methyl ester, 6),两个黄酮类化合物:槲皮素 (quercetin,7)和山奈酚 -3- β -D-半乳糖甙 (kaempferol 3- β -D-galactopyranoside,8)。这些化合物均是首次从该属植物中分离得到。

Rice 指出酚类化合物是一类主要的化感物质^[17]。在金钟藤的这些酚类成分中,化合物 1 和 7 是已知的化感物质。其中,化合物 1 具有抑制种子萌发和幼苗生长的作用^[18],还有较强的抗真菌活性^[19];化合物 7 有抑制植物生长和抗细菌的活性^[29]。值得

注意的是,咖啡酰基奎尼酸衍生物虽然对种子萌发和幼苗生长无影响[21-22],但对某些植物病原菌,如甘薯软腐病菌 (Rhizopus stolonifer) 具有抗菌作用[23],而且这类化合物对 HIV 和乙肝病毒具有抑制作用[24]。因此,我们推测:大量存在于入侵性杂草金钟藤、薇甘菊 (Mikania micrantha)[11] 和三裂蟛蜞菊 (Wedelia trilobata)[22]中的咖啡酰基奎尼酸衍生物可能与这些植物的抗病性有关。本研究说明金钟藤中亦有化感物质存在。

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