醉马草中黄酮类化学成分研究

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摘 要：目的 研究禾本科芨芨草属植物醉马草 *Achnatherum inebrians* 中的化学成分。**方法** 综合运用 HP-20 大孔树脂、ODS 中压色谱、Sephadex LH-20 凝胶柱色谱以及制备型高效液相色谱等方法进行系统的分离纯化，根据化合物的理化性质及其波谱数据，并通过对比文献报道的波谱数据，鉴定化合物的化学结构。**结果** 从醉马草乙醇提取物中分离得到 15 黄酮类化合物，分别鉴定为异红草素（**1**）、金丝桃苷（**2**）、槲皮素-3-*O*-β-*D*-吡喃葡萄糖基-(3′→*O*-3‴)-槲皮素-3″-*O*-β-*D*-吡喃半乳糖苷（**3**）、3′-甲氧基槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→6)-β-*D*-吡喃葡萄糖苷（**4**）、异鼠李素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷（**5**）、槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷（**6**）、槲皮素-3-*O*-β-*D*-吡喃葡萄糖基-7-*O*-α-*L*-吡喃鼠李糖苷（**7**）、山柰酚-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷（**8**）、山柰酚-3-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖苷（**9**）、8-甲氧基槲皮素-3-*O*-β-吡喃葡萄糖苷（**10**）、槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃半乳糖基-7-*O*-β-*D*-吡喃葡萄糖苷（**11**）、5,7,3′-三羟基-8,4′,5′-三甲氧基黄酮（**12**）、木犀草素-7-*O*-葡萄糖醛酸苷-6″-甲酯（**13**）、木犀草素-7-*O*-葡萄糖醛酸苷（**14**）和金圣草黄素（**15**）。**结论** 所有化合物均为首次从醉马草中分离得到。

关键词：醉马草；黄酮；异红草素；金丝桃苷；木犀草素-7-*O*-葡萄糖醛酸苷；金圣草黄素

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Flavonoids chemical constituents from *Achnatherum inebrians*

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Abstract: Objective To investigate the chemical constitutes from *Achnatherum inebrians*. **Methods** The compounds were isolated and purified by a combination of various chromatographic techniques including HP-20 macroporous resin, ODS MPLC, Sephadex LH-20, and semi-preparative HPLC. Their structures were identified by spectroscopic data and comparing the spectral data reported in literature. **Results** Fifteen compounds were isolated and identified from the ethanol extract of *A. inebrians* and their structures were elucidated as isoorientin (**1**), hyperoside (**2**), quercetin-3-*O*-β-*D*-glucopyranoside (3′→O-3‴)quercetin-3-*O*-β- *D*-galactopyranoside (**3**), 3'-*O*-methylquercetin-3-*O*-α-L-rhamnopyranosyl (1→6)-β-*D*-glucopyranoside (**4**)、isorhamnetin-3-*O*-α-*L*-rhamnopyranosyl (1→2)-β-*D*-glycopyranoside (**5**), quercetin-3-*O*-α-*L*-rhamnopyranosyl (1→2)-β-*D*-glucopyranoside (**6**), quercetin-3-*O*-β-*D*-glucopyranoside-7-*O*-α-*L*-rhamnopyranoside (**7**), kaempferol 3-*O*-α-L-rhamnopyranosyl (1→2)-β-*D*-glucopyranoside (**8**), kaempferol 3-*O*-α-*L*-rhamnopyranosyl (1→4)-β-*D*-glucopyranoside (**9**), 8-methoxyquercetin 3-*O*-β-glucoside (**10**), quercetin-3-*O*-α-*L*-rhamnopyranosyl(1→2)-β-*D*-galactopyranoside-7-*O*-β-*D*-glucopyranoside (**11**), 5,7,3′-trihydroxy-8,4′,5′-trimethoxyflavone (**12**), luteolin-7-*O*-glucuronide-6"-methyl ester (**13**), luteolin-7-*O*-glucuronide (**14**) and chrysoeriol (**15**). **Conclusion** All compounds are isolated from this plant for the first time.

Key words: *Achnatherum inebrians* (Hance) Keng.; flavonoids; isoorientin; hyperoside; luteolin-7-*O*-glucuronide; chrysoeriol

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醉马草 *Achnatherum inebrians* (Hance) Keng.为禾本科芨芨草属 *Achnatherum* Beauv.多年生草本植物。别名醉马芨芨、醉针茅、醉针草、马尿扫等，是我国西北草原上有名的毒草。醉马草在我国广泛分布于新疆、甘肃、青海、内蒙古等地，多生于海拔 1700～4200 m 的高山及亚高山草原、山坡草地和田边。醉马草是哈萨克医常用的药材，具有消肿止痛、清热解毒等功效，并对腮腺炎和关节疼痛的治疗都有很好的效果[1]。化学成分研究显示，醉马草中含有生物碱、黄酮等多种成分[2]。醉马草具有抗肿瘤、杀虫、抑菌等生物活性[3-5]。为了更合理地开发利用该植物资源，充分发挥应用价值，本实验对醉马草乙醇提取物中的化学成分进行系统研究，利用多种色谱分离方法共分离鉴定出 15 个黄酮类化合物，分别为异红草素（isoorientin，**1**）、金丝桃苷（hyperoside，**2**）、槲皮素-3-*O*-β-*D*-吡喃葡萄糖基-(3′→*O*-3‴)-槲皮素-3″-*O*-β-*D*-吡喃半乳糖苷[quercetin-3-*O*-β-*D*-glucopyranoside (3′→*O*-3‴)-quercetin-3-*O*-β-*D*-galactopyranoside，**3**]、3′-甲氧基槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→6)-β-*D*-吡喃葡萄糖苷 [3′-*O*-methylquercetin-3-*O*-α-*L*-rhamnopyranosyl (1→6)-β-*D*-glucopyranoside，**4**]、异鼠李素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷[isorhamnetin-3-*O*-α-*L*-rhamnopyranosyl-(1→2)-β-*D*-glycopyranoside，**5**]、槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷[quercetin-3-*O*-α-*L*-rhamnopyranosyl (1→2)-β-*D*-glucopyranoside，**6**]、槲皮素-3-*O*-β-*D*-吡喃葡萄糖基-7-*O*-α-*L*-吡喃鼠李糖苷（quercetin-3-*O*-β-*D*-glucopyranoside-7-*O*-α-*L*-rhamnopyranoside，**7**）、山柰酚-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷[kaempferol 3-*O*-α-*L*-rhamnopyranosyl (1→2)-β-*D*-glucopyranoside，**8**]、山柰酚-3-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖苷[kaempferol 3-*O*-α-*L*-rhamnopyranosyl (1→4)-β-*D*-glucopyranoside，**9**]、8-甲氧基槲皮素-3-*O*-β-吡喃葡萄糖苷（8-methoxyquercetin-3-*O*-β-glucoside，**10**）、槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃半乳糖基-7-*O*-β-*D*-吡喃葡萄糖苷[quercetin-3-*O*-α-*L*-rhamnopyranosyl-(1→2)-β-*D*-galactopyranoside-7-*O*-β-*D*-glucopyranoside，**11**]、5,7,3′-三羟基-8,4′,5′-三甲氧基黄酮（5,7,3′-trihydroxy-8,4′,5′-trimethoxyflavone，**12**）、木犀草素-7-*O*-葡萄糖醛酸苷-6″-甲酯（luteolin-7-*O*-glucuronide-6″-methyl ester，**13**）、木犀草素-7-*O*-葡萄糖醛酸苷（luteolin-7-*O*-glucuronide，**14**）和金圣草黄素（chrysoeriol，**15**）。所有化合物均为首次从该植物中分离得到。

1 仪器与材料

Bruker AVANCE III 500 型核磁共振仪（美国 Bruker-Biospin 公司）；Agilent 1100 LC/MSD TOF 型高分辨质谱仪（美国 Agilent 公司）；Agilent 1260 型高效液相色谱仪（美国 Agilent 公司）；Shimadzu LC-6AD 型半制备液相色谱仪（日本 Shimadzu 公司）；YMC ODS-A C_{18} 制备柱（250 mm×10 mm，5 μm，日本 YMC 公司）；Sephadex LH-20 葡聚糖凝胶色谱填料（瑞典 Pharmacia Fine Chemicals 公司）；MCI 色谱填料（日本三菱株式会社）。

醉马草于 2018 年 8 月采自青海省海东市平安区，经中国科学院西北高原生物研究所梅丽娟研究员鉴定为禾本科芨芨草属植物醉马草 *Achnatherum inebrians* (Hance) Keng.。

2 提取与分离

将阴干的醉马草全草粉碎（45 kg），然后经 80%乙醇回流提取（3×2 h），料液比 1∶8，得浸膏（约 3.2 kg）。浸膏经水分散后，依次用石油醚和醋酸乙酯萃取。所得水部位（1.5 kg）加水分散，上样 HP-20 大孔树脂，使用乙醇溶液梯度洗脱（0、20%、50%、70%、95%），得到 20 个流分 Fr. A～T。Fr. H（12.6 g）使用 ODS 中压柱色谱分离，甲醇-水（0∶10～10∶0）梯度洗脱，经 HPLC 分析后合并，共获得 12 个亚流分（Fr. H1～H12）。Fr. H9（200 mg）经 Sephadex LH-20 凝胶柱色谱（0～50%乙醇溶液梯度洗脱）、pre-HPLC（25%甲醇溶液）分离得到化合物 **1**（12 mg）、**3**（16 mg）、**10**（9 mg）和 **12**（7 mg）。Fr. H5（79 mg）经 Sephadex LH-20 凝胶柱色谱（10%～50%乙醇溶液梯度洗脱）得到化合物 **2**（25 mg）和 **14**（30 mg）。Fr. H2（153 mg）经 Sephadex LH-20 凝胶柱色谱（0～50%乙醇溶液梯度洗脱）、pre-HPLC（18%甲醇）分离得到化合物 **4**（5 mg）、**5**（17 mg）、**6**（6 mg）、**8**（8 mg）和 **9**（19 mg）。Fr. K（7.8 g）经 Sephadex LH-20 凝胶柱色谱（0～90%乙醇溶液梯度洗脱）分离得获得 30 个亚流分（Fr. K1～K30），Fr. K5（18 mg）经 pre-HPLC（21%甲醇）分离得到化合物 **7**（6 mg）。Fr. K9（156 mg）经 Sephadex LH-20 凝胶柱色谱（25%乙醇等度洗脱）得到化合物 **11**（26 mg）和 **13**（15 mg）。Fr. K17（60

mg）经 pre-HPLC（28%甲醇）分离得到化合物 **15**（11 mg）。

3 结构鉴定

化合物 **1**：黄色无定形粉末；ESI-MS *m*/*z*: 449 $[M+H]^+$，分子式为 $C_{21}H_{20}O_{11}$；^{1}H-NMR (500 MHz, methanol-d_4) δ: 7.34 (2H, overlapped, H-6′, 2′), 6.86 (1H, d, *J* = 8.0 Hz, H-5′), 6.51 (1H, s, H-3), 6.45 (1H, s, H-8), 4.84 (1H, overlapped, H-1″), 4.13 (1H, t, *J* = 9.0 Hz, H-2″), 3.83 (1H, d, *J* = 12.0 Hz, H-6″b), 3.69 (1H, dd, *J* = 12.0, 5.0 Hz, H-6″a), 3.43 (2H, overlapped, H-4″, 5″), 3.37 (1H, m, H-3″)；^{13}C-NMR (125 MHz, methanol-d_4) δ: 184.1 (C-4), 166.3 (C-2), 164.9 (C-7), 162.1 (C-5), 158.7 (C-9), 151.1 (C-4′), 147.1 (C-3′), 123.5 (C-1′), 120.3 (C-6′), 116.8 (C-2′), 114.1 (C-5′), 109.2 (C-6), 105.2 (C-3), 103.9 (C-10), 95.1 (C-8), 82.7 (C-5″), 80.1 (C-3″), 75.3 (C-1″), 72.5 (C-2″), 71.8 (C-4″), 62.9 (C-6″)。以上数据与文献报道的基本一致[6]，故鉴定化合物 **1** 为异红草素。

化合物 **2**：黄色晶针[氯仿-甲醇（1∶1）]；ESI-MS *m*/*z*: 465 $[M+H]^+$，分子式为 $C_{21}H_{20}O_{12}$；^{1}H-NMR (500 MHz, DMSO-d_6) δ: 12.66 (1H, s, 5-OH), 10.86 (1H, s, 7-OH), 9.77 (1H, s, 4′-OH), 9.19 (1H, s, 3′-OH), 7.68 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 7.53 (1H, d, *J* = 2.0 Hz, H-2′), 6.82 (1H, d, *J* = 8.5 Hz, H-5′), 6.41 (1H, d, *J* = 2.0 Hz, H-6), 6.21 (1H, d, *J* = 2.0 Hz, H-8), 5.39 (1H, d, *J* = 8.0 Hz, H-1″), 5.17 (1H, d, *J* = 4.5 Hz, 4″-OH), 4.90 (1H, d, *J* = 5.5 Hz, 2″-OH), 4.47 (2H, m, 3″, 6″-OH), 3.65 (1H, m, H-6″b), 3.57 (1H, m, H-6″a), 3.46 (1H, m, H-5″), 3.36 (1H, m, H-4″), 3.33 (1H, m, H-2″), 3.28 (1H, m, H-3″)；^{13}C-NMR (125 MHz, DMSO-d_6) δ: 177.5 (C-4), 164.2 (C-7), 161.3 (C-5), 156.3 (C-9), 156.3 (C-2), 148.5 (C-4′), 144.9 (C-3′), 133.5 (C-3), 122.1 (C-6′), 121.1 (C-1′), 116.0 (C-5′), 115.2 (C-2′), 104.0 (C-10), 101.8 (C-1″), 98.7 (C-6), 93.6 (C-8), 75.9 (C-5″), 73.2 (C-3″), 71.2 (C-2″), 68.0 (C-4″), 60.2 (C-6″)。以上数据与文献报道基本一致[7]，故鉴定化合物 **2** 为金丝桃苷。

化合物 **3**：棕色无定形粉末，ESI-MS *m*/*z*: 911 $[M+H]^+$，分子式为 $C_{42}H_{38}O_{23}$；^{1}H-NMR (500 MHz, methanol-d_4) δ: 7.81 (1H, d, *J* = 2.0 Hz, H-2‴), 7.67 (1H, d, *J* = 2.0 Hz, H-2′), 7.55 (1H, dd, *J* = 8.5, 2.0 Hz, H-5′), 7.53 (1H, dd, *J* = 8.5, 2.0 Hz, H-5‴), 6.83 (1H, d, *J* = 8.5 Hz, H-6‴), 6.81 (1H, d, *J* = 8.5 Hz, H-6′), 6.35 (2H, m, H-8, 8″), 6.15 (2H, s, H-6, 6″), 5.22 (1H, d, *J* = 7.5 Hz, H-1⁗), 5.13 (1H, d, *J* = 7.5 Hz, H-1⁗), 3.81 (1H, d, *J* = 3.0 Hz, H-4⁗), 3.78 (1H, t, *J* = 9.0 Hz, H-2⁗), 3.68 (1H, dd, *J* = 12.0, 2.0 Hz, H-6b⁗), 3.60 (1H, dd, *J* = 11.0, 6.0 Hz, H-6a⁗), 3.55～3.50 (3H, m, H-6b‴, 2⁗, 5⁗), 3.45 (2H, m, H-6a‴, 2‴), 3.39 (1H, t, *J* = 9.0 Hz, H-4‴), 3.31 (1H, t, *J* = 9.0 Hz, H-3‴), 3.19 (1H, m, H-5‴)；^{13}C-NMR (125 MHz, methanol-d_4) δ: 179.5 (C-4″), 179.5 (C-4), 166.0 (C-7), 166.0 (C-7″), 163.1 (C-5″), 163.0 (C-5), 159.0 (C-2), 158.7 (C-2″), 158.5 (C-9″), 158.4 (C-9), 150.0 (C-4‴), 149.8 (C-4′), 145.9 (C-3′), 145.8 (C-3‴), 135.7 (C-3″), 135.6 (C-3), 123.2 (C-6‴), 123.0 (C-6′), 122.9 (C-1′), 122.8 (C-1‴), 117.8 (C-2‴), 117.5 (C-2′), 116.1 (C-5′), 116.0 (C-5‴), 105.7 (C-10), 105.6 (C-10″), 105.4 (C-1⁗), 104.2 (C-1‴), 99.9 (C-6, 6″), 94.7 (C-8, 8″), 78.4 (C-5⁗), 78.1 (C-3‴), 77.2 (C-5⁗), 75.7 (C-2‴), 75.1 (C-3⁗), 73.2 (C-2⁗), 71.2 (C-4‴), 70.0 (C-4⁗), 62.5 (C-6‴), 61.9 (C-6⁗)。以上数据与文献报道基本一致[8]，故鉴定化合物 **3** 为槲皮素-3-*O*-β-*D*-吡喃葡萄糖基-(3′→*O*-3‴)-槲皮素-3″-*O*-β-*D*-吡喃半乳糖苷。

化合物 **4**：黄色无定形粉末，ESI-MS *m*/*z*: 625 $[M+H]^+$，分子式为 $C_{28}H_{32}O_{16}$；^{1}H-NMR (500 MHz, methanol-d_4) δ: 8.05 (1H, d, *J* = 2.0 Hz, H-2′), 7.46 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 6.85 (1H, d, *J* = 8.5 Hz, H-5′), 6.33 (1H, s, H-8), 6.11 (1H, d, *J* = 2.0 Hz, H-6), 5.83 (1H, d, *J* = 8.0 Hz, H-1″), 5.10 (1H, d, *J* = 1.0 Hz, H-1‴), 0.79 (3H, d, *J* = 6.5 Hz, H-6‴)；^{13}C-NMR (125 MHz, methanol-d_4) δ: 179.3 (C-4), 165.6 (C-7), 163.2 (C-5), 158.3 (C-2), 158.1 (C-9), 150.5 (C-3′), 148.4 (C-4′), 134.4 (C-3), 123.3 (C-6′), 123.1 (C-1′), 115.9 (C-5′), 114.6 (C-2′), 106.0 (C-10), 102.5 (C-1″), 100.1 (C-1‴), 99.6 (C-6), 94.5 (C-8), 77.9 (C-3″), 77.1 (C-5″), 75.6 (C-2″), 73.9 (C-4‴), 72.4 (C-4″), 72.3 (C-3‴), 70.6 (C-2‴), 69.8 (C-5‴), 68.3 (C-6″), 57.1 (-OCH_3), 17.4 (C-6‴)。以上数据与文献报道基本一致[9]，故鉴定化合物 **4** 为 3′-甲氧基槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→6)-β-*D*-吡喃葡萄糖苷。

化合物 **5**：黄色无定形粉末，ESI-MS *m*/*z*: 625 $[M+H]^+$，分子式为 $C_{28}H_{32}O_{16}$；^{1}H-NMR (500 MHz, methanol-d_4) δ: 7.93 (1H, d, *J* = 2.0 Hz, H-2′), 7.49

(1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 6.85 (1H, d, *J* = 8.5 Hz, H-5′), 6.32 (1H, s, H-8), 6.12 (1H, d, *J* = 2.0 Hz, H-6), 5.85 (1H, d, *J* = 8.0 Hz, H-1″), 5.11 (1H, d, *J* = 1.0 Hz, H-1‴), 0.81 (3H, d, *J* = 6.5 Hz, H-6‴); ^{13}C-NMR (125 MHz, methanol-d_4) *δ*: 179.3 (C-4), 165.7 (C-7), 163.2 (C-5), 158.4 (C-2), 158.2 (C-9), 150.6 (C-3′), 148.3 (C-4′), 134.3 (C-3), 123.4 (C-6′), 123.3 (C-1′), 117.7 (C-5′), 116.0 (C-2′), 114.4 (C-10), 102.8 (C-1‴), 100.1 (C-1″), 99.7 (C-6), 94.5 (C-8), 80.3 (C-2″), 78.8 (C-3″), 78.4 (C-5″), 73.9 (C-4‴), 72.4 (C-3‴), 72.3 (C-2‴), 71.8 (C-4″), 69.9 (C-5‴), 62.4 (C-6″), 56.9 (-OCH_3), 17.4 (C-6‴)。以上数据与文献报道基本一致[10]，故鉴定化合物 **5** 为异鼠李素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷。

化合物 **6**：黄色无定形粉末，ESI-MS *m*/*z*: 611 [M＋H]$^+$，分子式为 $C_{27}H_{30}O_{16}$；^{1}H-NMR (500 MHz, methanol-d_4) *δ*: 7.62 (1H, d, *J* = 2.0 Hz, H-2′), 7.59 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 6.83 (1H, d, *J* = 8.5 Hz, H-5′), 6.36 (1H, s, H-8), 6.17 (1H, d, *J* = 2.0 Hz, H-6), 5.06 (1H, d, *J* = 7.5 Hz, H-1″), 4.47 (1H, d, *J* = 1.0 Hz, H-1‴), 3.76 (1H, dd, *J* = 11.0, 1.0 Hz, H-6″b), 3.59 (1H, m, H-2‴), 3.50 (1H, dd, *J* = 9.5, 3.0 Hz, H-3‴), 1.08 (3H, d, *J* = 6.5 Hz, H-6‴); ^{13}C-NMR (125 MHz, methanol-d_4) *δ*: 179.4 (C-4), 166.1 (C-7), 163.0 (C-5), 159.3 (C-9), 158.5 (C-2), 149.8 (C-4′), 145.8 (C-3′), 135.6 (C-3), 123.5 (C-6′), 123.1 (C-1′), 117.7 (C-2′), 116.0 (C-5′), 105.7 (C-10), 104.7 (C-1″), 102.4 (C-1‴), 99.9 (C-6), 94.8 (C-8), 78.1 (C-3″), 77.2 (C-5″), 75.7 (C-2″), 73.9 (C-4‴), 72.2 (C-3‴), 72.1 (C-2‴), 71.4 (C-4″), 69.7 (C-5‴), 68.5 (C-6″), 17.9 (C-6‴)。以上数据与文献报道基本一致[11]，故鉴定化合物 **6** 为槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷。

化合物 **7**：黄色无定形粉末，ESI-MS *m*/*z*: 611 [M＋H]$^+$，分子式为 $C_{27}H_{30}O_{16}$；^{1}H-NMR (500 MHz, methanol-d_4) *δ*: 7.66 (1H, d, *J* = 2.0 Hz, H-2′), 7.53 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 6.82 (1H, d, *J* = 8.5 Hz, H-5′), 6.31 (1H, s, H-8), 6.10 (1H, d, *J* = 2.0 Hz, H-6), 5.72 (1H, d, *J* = 7.5 Hz, H-1″), 5.16 (1H, d, *J* = 1.0 Hz, H-1‴), 0.87 (3H, d, *J* = 6.5 Hz, H-6‴); ^{13}C-NMR (125 MHz, methanol-d_4) *δ*: 179.4 (C-4), 165.7 (C-7), 163.1 (C-5), 158.3 (C-9), 158.1 (C-2), 149.6 (C-4′), 145.9 (C-3′), 134.6 (C-3), 123.3 (C-6′), 123.0 (C-1′), 117.3 (C-2′), 116.1 (C-5′), 105.9 (C-10), 102.6 (C-1‴), 100.8 (C-1″), 99.6 (C-6), 94.4 (C-8), 77.5 (C-3″), 77.1 (C-5″), 75.7 (C-2″), 74.0 (C-4‴), 72.4 (C-3‴), 72.3 (C-2‴), 70.9 (C-5‴), 69.8 (C-4″), 62.0 (C-6″), 17.3 (C-6‴)。以上数据与文献报道的基本一致[12]，故鉴定化合物 **7** 为槲皮素-3-*O*-β-*D*-吡喃葡萄糖基-7-*O*-α-*L*-吡喃鼠李糖苷。

化合物 **8**：黄色无定形粉末，ESI-MS *m*/*z*: 595 [M＋H]$^+$，分子式为 $C_{27}H_{30}O_{15}$；^{1}H-NMR (500 MHz, methanol-d_4) *δ*: 8.03 (2H, d, *J* = 8.5 Hz, H-2′, 6′), 6.84 (2H, d, *J* = 8.5 Hz, H-3′, 5′), 6.33 (1H, d, *J* = 2.0 Hz, H-8), 6.12 (1H, d, *J* = 2.0 Hz, H-6), 5.67 (1H, d, *J* = 7.5 Hz, H-1″), 5.16 (1H, d, *J* = 1.0 Hz, H-1‴), 3.97 (1H, m, H-5‴), 3.94 (1H, m, H-2‴), 3.90 (1H, dd, *J* = 9.5, 7.5 Hz, H-3‴), 3.78 (1H, m, H-6″a), 3.72 (1H, dd, *J* = 9.5, 3.0 Hz, H-3″), 3.66 (1H, dd, *J* = 9.5, 3.0 Hz, H-2″), 3.59 (1H, m, H-4″), 3.54 (1H, m, H-5″), 3.45 (1H, t, *J* = 6.0 Hz, H-4‴), 3.29 (1H, m, H-6″b), 0.88 (1H, d, *J* = 6.5 Hz, H-6‴); ^{13}C-NMR (125 MHz, methanol-d_4) *δ*: 179.5 (C-4), 165.6 (C-7), 163.2 (C-5), 161.3 (C-4′), 158.4 (C-9), 158.4 (C-2), 134.4 (C-3), 132.2 (C-2′, 6′), 123.0 (C-1′), 116.1 (C-3′, 5′), 105.9 (C-10), 102.6 (C-1‴), 100.6 (C-1″), 99.6 (C-6), 94.5 (C-8), 79.6 (C-2″), 77.0 (C-3″), 75.8 (C-5″), 74.0 (C-4‴), 72.4 (C-2‴), 72.3 (C-3‴), 70.8 (C-4″), 69.8 (C-5‴), 62.2 (C-6″), 17.2 (C-6‴)。以上数据与文献报道的基本一致[13]，故鉴定化合物 **8** 为山柰酚-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷。

化合物 **9**：黄色无定形粉末，ESI-MS *m*/*z*: 595 [M＋H]$^+$，分子式为 $C_{27}H_{30}O_{15}$；^{1}H-NMR (500 MHz, methanol-d_4) *δ*: 8.01 (2H, d, *J* = 8.5 Hz, H-2′, 6′), 6.85 (2H, d, *J* = 8.5 Hz, H-3′, 5′), 6.34 (1H, d, *J* = 2.0 Hz, H-8), 6.14 (1H, d, *J* = 2.0 Hz, H-6), 5.71 (1H, d, *J* = 7.5 Hz, H-1″), 5.18 (1H, d, *J* = 1.0 Hz, H-1‴), 0.90 (1H, d, *J* = 6.5 Hz, H-6‴); ^{13}C-NMR (125 MHz, methanol-d_4) *δ*: 179.4 (C-4), 165.6 (C-7), 163.2 (C-5), 161.3 (C-4′), 158.5 (C-9), 158.4 (C-2), 134.4 (C-3), 132.1 (C-2′, 6′), 123.1 (C-1′), 116.1 (C-3′, 5′), 106.0 (C-10), 102.6 (C-1‴), 100.2 (C-1″), 99.7 (C-6), 94.5 (C-8), 80.1 (C-4″), 78.9 (C-5″), 78.4 (C-3″), 74.0 (C-4‴), 72.4 (C-2‴), 72.3 (C-3‴), 71.8 (C-2″), 69.9 (C-5‴), 62.6 (C-6″), 17.5 (C-6‴)。以上数据与文献报道基本一致[14]，故鉴定化合物 **9** 为山柰酚-3-*O*-α-*L*-

吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖苷。

化合物 **10**：黄色无定形粉末，ESI-MS *m*/*z*: 495 $[M+H]^+$，分子式为 $C_{22}H_{22}O_{13}$；^{1}H-NMR (500 MHz, methanol-d_4) δ: 7.87 (1H, d, J = 2.0 Hz, H-2′), 7.64 (1H, dd, J = 8.5, 2.0 Hz, H-6′), 6.84 (1H, d, J = 8.5 Hz, H-5′), 6.20 (1H, s, H-6), 5.16 (1H, d, J = 7.5 Hz, H-1″), 3.86 (3H, s, -OCH_3), 4.17 (1H, m, H-6″b), 3.78 (1H, m, H-6″a), 3.40～3.75 (5H, m, sugar-H)；^{13}C-NMR (125 MHz, methanol-d_4) δ: 178.4 (C-4), 164.7 (C-7), 158.6 (C-2), 158.0 (C-5), 150.3 (C-9), 148.5 (C-4′), 145.9 (C-3′), 135.7 (C-3), 129.1 (C-8), 123.0 (C-6′), 122.9 (C-1′), 117.7 (C-5′), 116.2 (C-2′), 105.3 (C-10), 100.1 (C-1″), 97.5 (C-6), 77.2 (C-3″), 75.1 (C-5″), 73.2 (C-2″), 70.0 (C-4″), 62.0 (-OCH_3), 61.9 (C-6″)。以上数据与文献报道基本一致[15]，故鉴定化合物 **10** 为 8-甲氧基槲皮素-3-*O*-β-吡喃葡萄糖苷。

化合物 **11**：黄色无定形粉末，ESI-MS *m*/*z*: 773 $[M+H]^+$，分子式为 $C_{33}H_{40}O_{21}$；^{1}H-NMR (500 MHz, DMSO-d_6) δ: 12.67 (1H, s, 5-OH), 7.61 (1H, dd, J = 8.5, 2.0 Hz, H-6′), 7.56 (1H, d, J = 2.0 Hz, H-2′), 6.85 (1H, d, J = 8.5 Hz, H-5′), 6.76 (1H, d, J = 2.0 Hz, H-8), 6.43 (1H, d, J = 2.0 Hz, H-6), 5.66 (1H, d, J = 7.5 Hz, H-1″), 5.09 (2H, m, H-1‴, 1⁗), 0.76 (1H, d, J = 6.5 Hz, H-6‴)；^{13}C-NMR (125 MHz, DMSO-d_6) δ: 177.5 (C-4), 162.8 (C-7), 160.9 (C-5), 156.9 (C-2), 156.0 (C-9), 148.6 (C-4′), 144.9 (C-3′), 133.2 (C-3), 121.8 (C-6′), 121.1 (C-1′), 116.3 (C-5′), 115.1 (C-2′), 105.7 (C-10), 100.5 (C-1‴), 99.7 (C-1⁗), 99.4 (C-6), 98.3 (C-1″), 94.3 (C-8), 77.7 (C-3⁗), 77.4 (C-5⁗), 77.2 (C-5″), 77.2 (C-2″), 76.4 (C-3″), 73.1 (C-2⁗), 71.9 (C-4‴), 70.7 (C-2‴), 70.6 (C-3‴), 70.3 (C-4⁗), 69.6 (C-5‴), 68.3 (C-4″), 61.0 (C-6⁗), 60.6 (C-6″), 17.3 (C-6‴)。以上数据与文献报道基本一致[16]，故鉴定化合物 **11** 为槲皮素-3-*O*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃半乳糖基-7-*O*-β-*D*-吡喃葡萄糖苷。

化合物 **12**：黄色无定形粉末，ESI-MS *m*/*z*: 361 $[M+H]^+$，分子式为 $C_{18}H_6O_8$；^{1}H-NMR (500 MHz, methanol-d_4) δ: 7.22 (1H, d, J = 2.0 Hz, H-2′), 7.18 (1H, d, J = 2.0 Hz, H-6′), 6.98 (1H, s, H-3), 6.30 (1H, s, H-6), 3.89 (3H, s, 5′-OCH_3), 3.96 (3H, s, 4′-OCH_3), 3.77 (3H, s, 8-OCH_3)；^{13}C-NMR (125 MHz, methanol-d_4) δ: 181.8 (C-4), 162.8 (C-2), 156.9 (C-7), 155.9 (C-5), 153.4 (C-5′), 150.6 (C-3′), 149.6 (C-9), 139.7 (C-4′), 127.6 (C-8), 125.9 (C-1′), 107.3 (C-3), 104.6 (C-6′), 103.6 (C-10), 102.3 (C-2′), 98.9 (C-6), 61.2 (8-OCH_3), 60.1 (4′-OCH_3), 56.1 (5′-OCH_3)。以上数据与文献报道基本一致[17]，故鉴定化合物 **12** 为 5,7,3′-三羟基-8,4′,5′-三甲氧基黄酮。

化合物 **13**：黄色无定形粉末，ESI-MS *m*/*z*: 477 $[M+H]^+$，分子式为 $C_{22}H_{20}O_{12}$；^{1}H-NMR (500 MHz, DMSO-d_6) δ: 7.23 (1H, dd, J = 8.5, 2.0 Hz, H-6′), 7.11 (1H, d, J = 2.0 Hz, H-2′), 6.76 (1H, d, J = 8.5 Hz, H-5′), 6.83 (1H, s, H-3), 6.76 (1H, d, J = 2.0 Hz, H-8), 6.66 (1H, d, J = 2.0 Hz, H-6), 4.99 (1H, d, J = 7.5 Hz, H-1″), 3.30～4.10 (4H, overlapped, H-2″～5″), 3.54 (3H, s, -OCH_3)；^{13}C-NMR (125 MHz, DMSO-d_6) δ: 182.0 (C-4), 169.2 (C-6″), 164.2 (C-2), 162.5 (C-7), 161.2 (C-5), 157.0 (C-9), 151.3 (C-4′), 146.8 (C-3′), 122.9 (C-1′), 118.9 (C-6′), 113.1 (C-2′), 112.2 (C-5′), 105.6 (C-10), 103.9 (C-3), 99.4 (C-1″), 99.1 (C-6), 94.6 (C-8), 75.4 (C-5″), 75.2 (C-3″), 72.7 (C-2″), 71.3 (C-4″), 55.8 (-OCH_3)。以上数据与文献报道基本一致[18]，故鉴定化合物 **13** 为木犀草素-7-*O*-葡萄糖醛酸苷-6″-甲酯。

化合物 **14**：黄色无定形粉末，ESI-MS *m*/*z*: 463 $[M+H]^+$，分子式为 $C_{21}H_{18}O_{12}$；^{1}H-NMR (500 MHz, DMSO-d_6) δ: 7.43 (1H, d, J = 2.0 Hz, H-2′), 7.41 (1H, dd, J = 8.5, 2.0 Hz, H-6′), 6.88 (1H, d, J = 2.0 Hz, H-5′), 6.77 (1H, d, J = 2.0 Hz, H-8), 6.72 (1H, s, H-3), 6.42 (1H, d, J = 2.0 Hz, H-6), 5.11 (1H, d, J = 7.5 Hz, H-1″), 3.70 (1H, d, J = 10.0 Hz, H-3″), 3.14 (1H, overlapped, H-2″), 3.30 (1H, overlapped, H-4″), 3.35 (1H, overlapped, H-5″)；^{13}C-NMR (125 MHz, DMSO-d_6) δ: 181.9 (C-4), 172.4 (C-6″), 164.5 (C-2), 162.9 (C-7), 161.0 (C-5), 157.0 (C-9), 150.2 (C-4′), 145.9 (C-3′), 121.2 (C-1′), 119.1 (C-6′), 116.1 (C-5′), 113.5 (C-2′), 105.3 (C-10), 103.7 (C-3), 99.6 (C-1″), 99.5 (C-6), 94.5 (C-8), 76.3 (C-3″), 74.2 (C-5″), 72.9 (C-2″), 71.9 (C-4″)。以上数据与文献报道基本一致[19]，故鉴定化合物 **14** 为木犀草素-7-*O*-葡萄糖醛酸苷。

化合物 **15**：黄色无定形粉末，ESI-MS *m*/*z*: 301 $[M+H]^+$，分子式为 $C_{16}H_{12}O_6$；^{1}H-NMR (500 MHz, DMSO-d_6) δ: 7.57 (1H, d, J = 2.0 Hz, H-2′), 7.56 (1H, dd, J = 8.5, 2.0 Hz, H-6′), 6.93 (1H, d, J = 2.0 Hz, H-5′), 6.91 (1H, s, H-3), 6.51 (1H, d, J = 2.0 Hz, H-8),

6.19 (1H, d, *J* = 2.0 Hz, H-6), 3.89 (3H, s, -OCH_3)；^{13}C-NMR (125 MHz, DMSO-d_6) δ: 181.8 (C-4), 164.2 (C-7), 163.7 (C-2), 161.4 (C-5), 157.3 (C-9), 150.7 (C-3′), 148.0 (C-4′), 121.5 (C-6′), 120.4 (C-1′), 115.8 (C-5′), 110.2 (C-2′), 103.7 (C-3), 103.2 (C-10), 98.8 (C-6), 94.1 (C-8), 56.0 (-OCH_3)。以上数据与文献报道基本一致[20]，故鉴定化合物 **15** 为金圣草黄素。

利益冲突 所有作者均声明不存在利益冲突

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