百蕊草化学成分分离

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［摘要］ **目的**：研究百蕊草的化学成分。**方法**：对百蕊草 95% 乙醇提取物采用各种柱色谱方法分离纯化，通过理化常数测定和光谱分析鉴定化合物结构。**结果**：从百蕊草中分离纯化了 10 个化合物，分别鉴定为木犀草素-7-*O*-葡萄糖苷（**1**），芹菜素-7-*O*-葡萄糖苷（**2**），芦丁（**3**），芹菜素-8-*C*-α-*L*-阿拉伯糖苷（**4**），高车前苷（**5**），大蓟苷（**6**），蒙花苷（**7**），芹菜素-7-*O*-β-*D*-葡萄糖醛酸苷（**8**），柯伊利素-7-*O*-β-*D*-葡萄糖醛酸苷（**9**），金圣草黄素（**10**）。**结论**：化合物 **10** 为首次从百蕊草属植物中分离得到，化合物 **4**～**9** 为首次从檀香科植物中分离得到。

［关键词］ 百蕊草；檀香科；高车前苷；大蓟苷；蒙花苷；金圣草黄素
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Isolation of Chemical Components from *Thesium chinense*

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［**Abstract**］ **Objective**: To investigate the chemical components of *Thesium chinense*. **Method**: Various column chromatography methods were used to isolate and purify the compounds from 95% ethanol extracts of *T. chinense*, and their structures were identified by physico-chemical and spectral analysis. **Result**: Ten compounds were isolated from *T. chinense* and identified as luteolin-7-*O*-glucoside (**1**), apigenin-7-*O*-glucoside (**2**), rutin (**3**), apigenin-8-C-α-*L*-arabinopyranoside (**4**), homoplantaginin (**5**), pectolinarin (**6**), linarin (**7**), apigenin-7-*O*-β-*D*-glucopyranuronide (**8**), chrysoeriol 7-*O*-glucuronide (**9**) and chrysoeriol (**10**). **Conclusion**: Compound **10** was isolated from the genus *Thesium* for the first time and compounds **4-9** were isolated from the family Santalaceae for the first time.

［**Key words**］ *Thesium chinense*; Santalaceae; homoplantaginin; pectolinarin; linarin; chrysoeriol

百蕊草，又名百乳草、地石榴、细须草，全国均有分布。全草入药，有清热解毒，补肾涩精之功效。百蕊草含有黄酮、有机酸、生物碱、甾醇、酚类、挥发油等多种化学成分，临床主要用于治疗肺炎，咽炎，急性乳腺炎，急性扁桃体炎等[1-2]。

目前，国内市场有百蕊草片剂、颗粒剂、糖浆剂等多种剂型，然而百蕊草化学成分研究尚不完善，仅有百蕊草素等[3]少数化合物被报道，为了进一步了解其物质基础，本研究对百蕊草进行了系统的化学成分分离鉴定，从百蕊草的乙醇提取物中分离得到 10 个化合物，其中化合物 **10** 为首次从百蕊草属植物中分离得到，化合物 **4**～**9** 为首次从檀香科植物中分离得到。

1 材料

AVANCE III 400 和 600 型核磁共振波谱仪（瑞士瑞士布鲁克公司，四甲基硅烷 TMS 为内标），MAT-95 型质谱仪（Finnigan 公司），LC3000 型制备高效液相色谱仪（北京创新通恒科技有限公司），薄层色谱和柱色谱硅胶（200～300 目，青岛美高集团有限公司）；小孔树脂凝胶柱（MCI，CHP20P，75～100 μm，日本三菱化学有限公司），羟丙基葡聚糖凝胶（Sephadex LH-20，25～100 μm，美国 GE 公司），

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YMC 凝胶(ODS-A-HG, 50 μm,日本 YMC 有限公司);甲醇色谱纯,水为超纯水,其他试剂均为分析纯。

百蕊草于 2013 年 9 月购自安徽亳州药材市场,经第二军医大学张汉明教授鉴定为檀香科植物百蕊草 *Thesium chinense* 的干燥全草,标本保存于第二军医大学药学院标本室。

2 提取和分离

干燥百蕊草药材 3.5 kg,粉碎,用 95% 乙醇回流提取 3 次,每次 2 h,过滤合并滤液并减压浓缩至无醇味,得乙醇提取物 326 g。分别用石油醚、乙酸乙酯萃取 3 次,减压浓缩回收溶剂后得石油醚部位浸膏 28 g,乙酸乙酯部位浸膏 258 g。乙酸乙酯部位首先进行 MCI 凝胶柱色谱(甲醇0∶1 ~ 1∶0),得到 6 个流份 (Fr. 1 ~ Fr. 6)。Fr. 2 经 Sephadex LH-20 (甲醇-水 0∶1 ~ 8∶2) 后,进行 YMC (甲醇-水 1∶9 ~ 6∶4) 柱色谱或半制备高效液相色谱 (甲醇-水 3∶7,检测波长 254 nm),得到芹菜素-7-*O*-葡萄糖苷(43 mg),木犀草素-7-*O*-葡萄糖苷(14 mg) 及芦丁(8 mg)。Fr. 3 (29.1 g) 依次经硅胶 (CH_2Cl_2-甲醇 30∶1 ~ 3∶1),Sephadex LH-20(甲醇) 及 YMC (甲醇-水 3∶7 ~ 9∶1) 柱色谱得芹菜素-8-C-α-*L*-阿拉伯糖苷(11 mg),高车前苷(7 mg) 和大蓟苷(7 mg)。Fr. 4 进一步经 Sephadex-LH 20(甲醇-水,3∶7 ~ 5∶5) 得蒙花苷(5 mg),芹菜素-7-*O*-β-*D*-葡萄糖醛酸苷(8 mg) 和柯伊利素-7-O-β-*D*-葡萄糖醛酸苷(6 mg)。Fr. 5 经硅胶 (CH_2Cl_2-甲醇,30∶1 ~ 7∶1) 得金圣草黄素(5 mg)。

3 结构鉴定

化合物 **1** 黄色粉末,盐酸-镁粉反应阳性,ESI-MS *m/z* 449.1 [M + H]$^-$。^{1}H-NMR (600 MHz, DMSO) δ: 6.75 (1H, s, H-3), 6.45 (1H, d, *J* = 2.1 Hz, H-6), 6.79 (1H, d, *J* = 2.1 Hz, H-8), 7.42 (1H, d, *J* = 2.2 Hz, H-2′), 6.91 (1H, d, *J* = 8.3 Hz, H-5′), 7.45 (1H, dd, *J* = 8.3, 2.2 Hz, H-6′), 5.08 (1H, d, *J* = 7.5 Hz, H-1″), 3.18 ~ 3.72 (5H, m, H-2″ ~ 6″), 12.99 (5-OH), 9.40 (3′-OH), 10.00 (4′-OH); ^{13}C-NMR (150 MHz, DMSO) δ: 164.5 (C-2), 103.1 (C-3), 181.7 (C-4), 161.1 (C-5), 99.5 (C-6), 162.9 (C-7), 94.7 (C-8), 156.9 (C-9), 105.3 (C-10), 121.4 (C-1′), 113.5 (C-2′), 145.7 (C-3′), 149.8 (C-4′), 116.0 (C-5′), 119.1 (C-6′), 100.3 (C-1″), 73.1 (C-2″), 76.4 (C-3″), 69.6 (C-4″), 77.1 (C-5″), 60.6 (C-6″)。以上波谱数据与文献[4]对照,鉴定为木犀草素-7-*O*-葡萄糖苷。

化合物 **2** 黄色粉末,盐酸-镁粉反应阳性,ESI-MS *m/z* 433 [M + H]$^-$。^{1}H-NMR (400 MHz, DMSO) δ: 7.92 (2H, d, *J* = 8.3 Hz, H-2′, 6′), 6.93 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 6.84 (1H, s, H-3), 6.82 (1H, d, *J* = 1.5 Hz, H-8), 6.43 (1H, d, *J* = 1.5 Hz, H-6), 5.10 (1H, d, *J* = 7.3 Hz, H-1″), 3.18 ~ 3.68 (4H, m, H-2″, 3″, 4″, 5″); ^{13}C-NMR (100 MHz, DMSO) δ: 164.3 (C-2), 102.8 (C-3), 181.7 (C-4), 161.5 (C-5), 99.5 (C-6), 162.9 (C-7), 94.7 (C-8), 156.9 (C-9), 105.3 (C-10), 121.4 (C-1′), 113.5 (C-2′), 145.7 (C-3′), 149.8 (C-4′), 116.0 (C-5′), 119.1 (C-6′), 100.4 (C-1″), 73.2 (C-2″), 76.5 (C-3″), 69.7 (C-4″), 77.1 (C-5″), 61.0 (C-6″)。以上波谱数据与文献[5]对照,鉴定该化合物为芹菜素-7-*O*-葡萄糖苷。

化合物 **3** 淡黄色针晶,盐酸-镁粉反应阳性,Molish 反应阳性,ESI-MS *m/z* 611.5 [M + H]$^-$。^{1}H-NMR (400 MHz, DMSO) δ: 7.93 (1H, d, *J* = 2.2 Hz, H-2′), 7.54 (1H, dd, *J* = 8.3 Hz, H-6′), 6.89 (2H, d, H-5′), 6.11 (1H, d, *J* = 2.0 Hz, H-6), 6.20 (1H, d, *J* = 2.0 Hz, H-8), 5.72 (1H, d, *J* = 7.6 Hz, H-1″), 5.20 (1H, d, *J* = 1.4 Hz, H-1‴), 3.00 ~ 4.00 (H-2″, 3″, 4″, 5″, 2‴, 3‴, 4‴, 5‴), 1.07 (3H, d, *J* = 6.2 Hz, CH_3-6‴); ^{13}C-NMR (100 MHz, DMSO) δ: 156.4 (C-2), 133.3 (C-3), 177.4 (C-4), 161.2 (C-5), 98.7 (C-6), 164.2 (C-7), 93.8 (C-8), 156.6 (C-9), 104.0 (C-10), 121 (C-1′), 115.2 (C-2′), 116.3 (C-3′), 148.4 (C-4′), 116.3 (C-5′), 121.7 (C-6′), 101.2 (C-1″), 73.9 (C-2″), 76.2 (C-3″), 70.7 (C-4″), 76.0 (C-5″), 67 (C-6″), 100.7 (C-1‴), 70.4 (C-2‴), 70.2 (C-3‴), 71.7 (C-4‴), 68.2 (C-5‴), 17.7 (C-6‴)。以上波谱数据与文献[6]对照,鉴定化合物 **3** 为芸香苷,即芦丁。

化合物 **4** 黄色无定形粉末,ESI-MS *m/z* 419.1 [M + H]$^-$。^{1}H-NMR (600 MHz, DMSO) δ: 6.82 (1H, s, H-3), 6.26 (1H, s, H-6), 8.21 (2H, br s, H-2′, 6′), 6.89 (2H, d, *J* = 8.9 Hz, H-3′, 5′), 13.29 (1H, s, OH-5), 4.61 (1H, d, *J* = 9.3 Hz, H-1″); ^{13}C-NMR (150 MHz, DMSO) δ: 164.6 (C-2), 102.5 (C-3), 182.6 (C-4), 161.0 (C-5), 99.0 (C-6), 163.5 (C-7), 105.0 (C-8), 156.4 (C-9), 104.3 (C-10), 121.6 (C-1′), 129.9 (C-2′, 6′), 116.6 (C-3′, 5′), 161.6 (C-4′), 75.1 (C-1″), 68.8 (C-2″), 75.3 (C-

3″),69.6 (C-4″),71.5 (C-5″)。以上波谱数据与文献[7]比对,鉴定化合物**4** 为芹菜素-8-C-α-*L*-阿拉伯糖苷。

化合物**5** 黄色无定形粉末,ESI-MS *m/z* 463.1 [M + H]$^-$。^{1}H-NMR (600 MHz, DMSO) δ: 6.85 (1H,s,H-3),7.00 (1H,s,H-8),7.95 (2H,d,*J* = 8.8 Hz,H-2′,6′),6.93 (2H,d,*J* = 8.8 Hz,H-3′,5′),3.76 (3H,s,6-OCH_3),12.95 (1H,s,OH-5),5.12 (1H,d,*J* = 7.2 Hz,Glc-1),3.21 (1H,t,*J* = 8.7 Hz,Glc-2),3.31 ~ 3.51 (4H,m,Glc-3,4,5,6a),3.74 (1H,br d,*J* = 10.7 Hz,Glc-6b);^{13}C-NMR (150 MHz,DMSO) δ: 164.5 (C-2),102.8 (C-3),182.3 (C-4),152.7 (C-5),132.2 (C-6),156.4 (C-7),94.5 (C-8),152.7 (C-9),105.8 (C-10),121.2 (C-1′),128.9 (C-2′,6′),116.3 (C-3′,5′),161.0 (C-4′),60.3 (OMe-6),100.2 (Glc-1),73.5 (Glc-2),77.4 (Glc-3),69.8 (Glc-4),77.0 (Glc-5),60.8 (Glc-6)。结合文献[8]波谱数据鉴定该化合物结构为高车前苷。

化合物**6** 黄色无定形粉末,ESI-MS *m/z* 623.6 [M + H]$^-$。^{1}H-NMR (600 MHz, DMSO) δ: 6.97 (1H,s,H-3),6.95 (1H,s,H-8),8.07 (2H,d,*J* = 8.8 Hz,H-2′,6′),7.19 (2H,d,*J* = 8.8 Hz,H-3′,5′),3.88 (3H,s,OCH_3-4′),3.77 (3H,s,OCH_3-6),12.95 (1H,s,OH-5),5.12 (1H,d,*J* = 7.0 Hz,H-1″),4.56 (1H,br s,H-1‴),1.05 (3H,d,*J* = 6.2 Hz,H-6‴);^{13}C-NMR (150 MHz,DMSO) δ: 164.1 (C-2),103.5 (C-3),182.4 (C-4),152.3 (C-5),132.8 (C-6),152.6 (C-7),94.5 (C-8),156.6 (C-9),106.1 (C-10),122.8 (C-1′),128.5 (C-2′,6′),115.0 (C-3′,5′),162.5 (C-4′),60.3 (OCH_3-6),55.8 (OCH_3-4′),100.5 (C-1″),73.4 (C-2″),76.6 (C-3″),69.7 (C-4″),76.0 (C-5″),66.1 (C-6″),100.5 (C-1‴),70.8 (C-2‴),71.1 (C-3‴),72.1 (C-4‴),68.3 (C-5‴),18.1 (C-6‴)。结合文献[9]波谱数据鉴定该化合物结构为大蓟苷。

化合物**7** 淡黄色粉末,ESI-MS *m/z* 593.2 [M + H]$^-$。^{1}H-NMR (400 MHz, DMSO) δ: 13.05 (1H,br s,5-OH),8.03 (2H,d,*J* = 8.9 Hz,H-2′,6′),7.17 (2H,d,*J* = 9.0 Hz,H-3′,5′),6.95 (1H,s,H-3),6.86 (1H,d,*J* = 2.1 Hz,H-8),6.59 (1H,d,*J* = 2.0 Hz,H-6),5.26 (1H,d,*J* = 7.2 Hz,H-1″ of Glc),4.82 (1H,br s,H-1‴ of Rha),3.84 (3H,s,4′-OCH_3),1.19 (3H,d,*J* = 6.2 Hz,6‴-CH_3);^{13}C-NMR (100 MHz, DMSO) δ: 164.2 (C-2),104.3 (C-3),182.3 (C-4),162.7 (C-5),100.2 (C-6),163.5 (C-7),95.1 (C-8),157.4 (C-9),105.9 (C-10),123.0 (C-1′),128.7 (C-2′,6′),114.9 (C-3′,C-5′),161.7 (C-4′);Glc: 101.2 (C-1″),73.7 (C-2″),76.4 (C-3″),70.9 (C-4″),76.9 (C-5″),66.7 (C-6″);Rha: 100.6 (C-1‴),71.5 (C-2‴),70.3 (C-3‴),72.8 (C-4‴),68.9 (C-5‴),18.1 (C-6‴),55.7 (OCH_3)。以上波谱数据与文献[10]比对,鉴定化合物**4** 为蒙花苷。

化合物**8** 淡黄色粉末,ESI-MS *m/z* 461.1 [M + H]$^-$。^{1}H-NMR (400 MHz, DMSO) δ: 12.97 (1H,br s,5-OH),7.93 (2H,d,*J* = 8.3 Hz,H-2′,6′),6.92 (2H,d,*J* = 8.4 Hz,H-3′,5′),6.84 (1H,s,H-3),6.81 (1H,d,*J* = 1.5 Hz,H-8),6.43 (1H,d,*J* = 1.5 Hz,H-6),5.10 (1H,d,*J* = 7.3 Hz,H-1″),3.17 ~ 3.67 (4H,m,H-2″,3″,4″,5″);^{13}C-NMR (DMSO,100 MHz) δ: 164.4 (C-2),103.1 (C-3),182.1 (C-4),161.2 (C-5),99.7 (C-6),163.2 (C-7),94.8 (C-8),157.1 (C-9),105.4 (C-10),121 (C-1′),128.7 (C-2′),116.2 (C-3′),161.7 (C-4′),116.2 (C-5′),128.7 (C-6′),99.8 (C-1″),73.1 (C-2″),74.2 (C-3″),72.1 (C-4″),76.6 (C-5″),172.3 (C-6″)。结合文献[11]波谱数据鉴定该化合物为芹菜素-7-*O*-β-*D*-葡萄糖醛酸苷。

化合物**9** 淡黄色粉末,ESI-MS *m/z* 507.1 [M + H]$^-$。^{1}H-NMR (400 MHz, DMSO) δ: 12.97 (1H,br s,5-OH),7.57 (1H,dd,*J* = 8.4,1.8 Hz,H-6′),7.56 (1H,d,*J* = 1.8 Hz,H-2′),6.95 (1H,d,*J* = 8.4 Hz,H-5′),6.94 (1H,s,H-3),6.84 (1H,d,*J* = 2.1 Hz,H-8),6.43 (1H,d,*J* = 2.1 Hz,H-6),5.06 (1H,d,*J* = 7.1 Hz,H-1″),3.88 (3H,s,3′-OCH_3),3.15 ~ 3.58 (4H,m,H-2″,3″,4″,5″);^{13}C-NMR (100 MHz,DMSO) δ: 164.3 (C-2),103.5 (C-3),182.2 (C-4),161.2 (C-5),99.8 (C-6),163.3 (C-7),94.9 (C-8),157.1 (C-9),105.4 (C-10),121.3 (C-1′),110.4 (C-2′),148.3 (C-3′),151.4 (C-4′),116 (C-5′),120.7 (C-6′),99.8 (C-1″),73.1 (C-2″),76.8 (C-3″),72.2 (C-4″),73.8 (C-5″),171.9 (C-6″),56.1 (OCH_3)。以上波谱数据与文献[12]比对,鉴定化合物**9** 为柯伊利素-7-*O*-β-*D*-葡萄糖醛酸苷。

化合物**10** 淡黄色粉末,ESI-MS *m/z* 301.3 [M + H]$^-$。^{1}H-NMR (400 MHz, DMSO) δ: 12.97

(1H, br s, 5-OH), 7.57 (2H, m, H-6′, 2′), 6.94 (1H, d, J = 8.9 Hz, H-5′), 6.91 (1H, s, H-3), 6.50 (1H, d, J = 2.0 Hz, H-8), 6.19 (1H, d, J = 2.0 Hz, H-6), 3.90 (3H, s, OCH_3); ^{13}C-NMR (100 MHz, DMSO) δ: 163.8 (C-2), 103.8 (C-3), 182 (C-4), 157.6 (C-5), 99.1 (C-6), 164.7 (C-7), 94.3 (C-8), 161.6 (C-9), 103.4 (C-10), 120.6 (C-1′), 110.4 (C-2′), 151 (C-3′), 148.2 (C-4′), 116 (C-5′), 121.7 (C-6′), 56.2 (OCH_3)。以上波谱数据与文献[13]比对,故鉴定该化合物为金圣草黄素。

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