盔状黄芩中的苯乙醇苷及黄酮苷类化合物分析

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［摘要］ **目的**：研究盔状黄芩全草的化学成分。**方法**：取干燥的盔状黄芩全草，粉碎后用 95% 乙醇回流提取，减压浓缩得总浸膏。将浸膏悬浮于水中，依次用石油醚、三氯甲烷、乙酸乙酯、正丁醇进行萃取，得石油醚、三氯甲烷、乙酸乙酯和正丁醇部位，取乙酸乙酯部位分别用硅胶柱色谱，Sephadex LH-20 柱色谱及高效制备薄层等方法对盔状黄芩中的苷类化合物进行分离纯化，并根据理化性质和波谱数据对其化学结构进行阐明。**结果**：从乙酸乙酯部位共发现 11 个化合物，包括 9 个苯乙醇苷和 2 个黄酮苷，分别为 isocrenatoside（**1**），osmanthuside B_6（**2**），eutigoide A（**3**），plantainoside C（**4**），calceorioside B（**5**），isomartynoside（**6**），verbascoside（**7**），acteoside（**8**），desrhamnosyl acteoside（**9**），5，7-二羟基-8，2′-二甲氧基-7-*O*-*β*-*D*-葡萄糖苷（**10**），洋芹素-7-*O*-鼠李糖苷（**11**）。**结论**：化合物 **1**～**4**，**7**～**11** 为首次从该植物中发现；同时，文献调研发现，分离得到的 plantainoside C，洋芹素-7-*O*-鼠李糖苷等化合物具有一定的抗炎、抗氧化活性，为进一步开展盔状黄芩的药效物质基础研究及该药材的开发利用提供了很好的参考依据。

［关键词］ 黄芩属；盔状黄芩；苯乙醇苷；黄酮苷
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Analysis of Phenylethanoid Glycosides and Flavonoid Glycosides from *Scutellaria galericulata*

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［**Abstract**］ **Objective**: To investigate the chemical constituents of *Scutellaria galericulata*. **Method**: The herb of *S. galericulata* was crushed and then extracted with 95% ethanol. The extracts were combined and concentrated under reduced pressure. The extracts were dispersed in water and respectively extracted with petroleum ether, ethyl acetate, chloroform and *n*-butanol to get petroleum ether fraction, ethyl acetate fraction, chloroform fraction and *n*-butanolfraction. Ethyl acetate fraction were separated and purified by silica gel column chromatography, Sephadex LH-20 and HPTLC. The structures of the glycosides compounds were identified by their physico-chemical properties and spectral data. **Result**: Eleven compounds were isolated and purified as: isocrenatoside (**1**), osmanthuside B_6 (**2**), eutigoide A (**3**), plantainoside C (**4**), calceorioside B (**5**), isomartynoside (**6**), verbascoside (**7**), acteoside (**8**), desrhamnosyl acteoside (**9**), 5, 7-dihydroxy-8, 2′-

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dimethoxyflavone-7-*O*-β-*D*-glucopyranoside (**10**), and apigenin-7-*O*-rhamnoside (**11**). **Conclusion**: Compounds **1-4** and **7-11** were isolated from *S. galericulata* for the first time, and the literature review showed that plantainoside C, apigenin-7-*O*-rhamnoside and other compounds had anti-inflammatory and antioxidant activities, providing a good reference for further studies onpharmacodynamic material basis and the development and utilization of *S. galericulata*.

[**Key words**] *Scutellaria*; *S. galericulata*; phenylethanoid glycoside; flavonoid glycoside

盔状黄芩,国内主产于陕西、内蒙古、新疆等地,国外主要分布于欧洲各国、日本等国家。盔状黄芩性寒、味苦,归肺胆、脾胃、大肠经,具有清热解毒、活血止痛之功效;临床上主要用于治疗肝炎、淋症等疾病[1-2]。

前期实验中,课题组通过 Molish 反应对盔状黄芩 95% 乙醇提取物进行了分析,发现其乙酸乙酯部位含有苷类化合物。Ersoz 等[3]曾于 2002 年对产自土耳其的盔状黄芩进行研究,从中发现了 4 个苯乙醇苷。为此,课题组通过多种色谱分离技术,对盔状黄芩 95% 乙醇提取物中的苷类化合物进行了研究,从中发现了 11 个化合物,包括 9 个苯乙醇苷(化合物 **1** ~ **9**)和 2 个黄酮苷(化合物 **10**,**11**)。化合物 **1** ~ **4**,**7** ~ **11** 为首次从该植物中发现。

1 材料

XT-4 型微型熔点测定仪(温度未校正),Autospec-Ultima E TOF 型质谱仪,AVANCE Ⅲ™ 500 型核磁共振仪(四甲基硅烷内标,德国 Bruker 公司);聚酰胺(30 ~ 60 目,上海今瑞化工产品有限公司),LH-20 羟丙基葡聚糖凝胶(Sephadex LH-20,北京金欧亚进口分装产品),GF_{254} 薄层色谱、柱色谱硅胶(200 ~ 300 目)及高效制备薄层硅胶板(HPTLC,20 cm × 20 cm)均为青岛海洋化工厂产品。盔状黄芩全草采自新疆乌鲁木齐,由烟台大学药学院生药学教研室李桂生博士鉴定为唇形科植物盔状黄芩 *Scutellaria galericulata* 的干燥全草,标本(YP13065)保存于烟台大学药学院标本室。

2 提取和分离

取干燥的盔状黄芩全草 40.0 kg,粉碎后用 95% 乙醇回流提取 3 次,每次 1 h。提取液合并、减压浓缩,得总浸膏 2.8 kg。将浸膏悬浮于水中,依次用石油醚、三氯甲烷、乙酸乙酯、正丁醇反复萃取,萃取液分别合并、减压浓缩,得乙酸乙酯部位 225.3 g。乙酸乙酯部位首先过聚酰胺柱色谱,分别用去离子水,45% 乙醇洗脱,45% 乙醇洗脱液减压浓缩,得浸膏 89.8 g;浸膏通过硅胶柱色谱(10 cm × 120 cm),环己烷-丙酮梯度洗脱(90∶10 ~ 50∶50),分为 26 个组分。组分 22(13.5 g)通过 Sephadex LH-20 柱色谱洗脱[三氯甲烷-甲醇(1∶4)]及高效制备薄层展开[20 cm × 20 cm,三氯甲烷-甲醇(75∶15)]的反复分离与纯化,得化合物 **3** (82 mg),**5**(65 mg),**6**(31 mg);组分 24(16.1 g)通过 Sephadex LH-20 柱色谱[三氯甲烷-甲醇(1∶4)洗脱]与高效制备薄层[三氯甲烷-甲醇(80∶20)展开]的多次分离及纯化,得化合物 **1** (68 mg),**2**(132 mg),**4**(26 mg);组分 25(20.2 g)通过 Sephadex LH-20 柱色谱洗脱[三氯甲烷-甲醇(1∶4)]及高效制备薄层展开[三氯甲烷-甲醇(75∶25)]的多次分离及纯化,得化合物 **7**(43 mg),**8** (110 mg), **9** (64 mg), **10** (25 mg), **11** (163 mg)。

3 结构鉴定

化合物 **1** 黄色粉末(甲醇),mp 198 ~ 201 ℃。ESI-MS *m/z* 621.2 $[M + H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 6.75 (1H, d, *J* = 1.8 Hz, H-2), 6.70 (1H, d, *J* = 8.0 Hz, H-5), 6.60 (1H, dd, *J* = 1.8, 8.0 Hz, H-6), 4.52 (1H, m, H-7), 3.90 (1H, m, H_a-8), 3.69 (1H, m, H_b-8), 4.45 (1H, m, H-1′), 3.36 (1H, m, H-2′), 3.87 (1H, m, H-3′), 3.53 (1H, m, H-4′), 3.71 (1H, m, H-5′), 4.20 (1H, m, H_a-6′), 4.52 (1H, m, H_b-6′), 5.01 (1H, m, H-1″), 3.73 (1H, m, H-2″), 3.59 (1H, m, H-3″), 3.35 (1H, m, H-4″), 3.92 (1H, m, H-5″), 1.10 (3H, d, *J* = 6.2 Hz, H-6″), 7.10 (1H, d, *J* = 1.7 Hz, H-2‴), 6.78 (1H, d, *J* = 8.2 Hz, H-5‴), 7.02 (1H, dd, *J* = 1.7, 8.2 Hz, H-6‴), 7.48 (1H, d, *J* = 15.8 Hz, H-7‴), 6.29 (1H, d, *J* = 15.8 Hz, H-8‴); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 128.5 (C-1), 114.0 (C-2), 145.6 (C-3), 145.5 (C-4), 115.8 (C-5), 117.6 (C-6), 71.3 (C-7), 76.1 (C-8), 99.5 (C-1′), 80.8 (C-2′), 76.4 (C-3′), 71.3 (C-4′), 75.8 (C-5′), 63.7 (C-6′), 100.2 (C-1″), 72.5 (C-2″), 70.9 (C-3″), 70.8 (C-4″), 68.8 (C-5″), 18.4 (C-6″), 128.5 (C-1‴), 114.2 (C-2‴), 145.9 (C-3‴), 146.1 (C-4‴), 116.3 (C-5‴), 121.9 (C-6‴), 145.5 (C-7‴), 115.4

(C-8‴),168.3 (C-9‴)。以上数据与文献[4]报道的 isocrenatoside 的数据一致,故鉴定化合物 **1** 为 isocrenatoside。

化合物 **2** 黄色粉末(甲醇),mp 185 ~ 186 ℃。ESI-MS *m/z* 591.3 [M + H]$^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 7.01 (2H, d, *J* = 8.4 Hz, H-2, H-6), 6.63 (2H, d, *J* = 8.4 Hz, H-3, H-5), 2.73 (2H, t, *J* = 7.4, 14.8 Hz, H-7), 3.80 (1H, m, H_a-8), 3.91 (1H, m, H_b-8), 4.28 (1H, d, *J* = 7.8 Hz, H-1′), 3.52 (1H, m, H-2′), 3.80 (1H, m, H-3′), 3.16 (1H, m, H-4′), 3.71 (1H, m, H-5′), 4.21 (1H, m, H_a-6′), 4.39 (1H, m, H_b-6′), 7.50 (2H, d, *J* = 8.6 Hz, H-2″, H-6″), 6.81 (2H, d, *J* = 8.5 Hz, H-3″, H-5″), 7.55 (1H, d, *J* = 15.8 Hz, H-7″), 6.41 (1H, d, *J* = 15.8 Hz, H-8″), 5.15 (1H, s, H-1‴), 3.61 (1H, m, H-2‴), 3.79 (1H, m, H-3‴), 3.23 (1H, m, H-4‴), 3.92 (1H, m, H-5‴), 1.10 (3H, d, *J* = 6.1 Hz, H-6‴); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 130.2 (C-1), 116.5 (C-2), 131.9 (C-3), 156.8 (C-4), 131.9 (C-5), 116.5 (C-6), 36.3 (C-7), 72.1 (C-8), 102.5 (C-1′), 74.7 (C-2′), 84.0 (C-3′), 70.1 (C-4′), 75.2 (C-5′), 63.6 (C-6′), 127.6 (C-1″), 131.8 (C-2″), 116.4 (C-3″), 161.3 (C-4″), 116.4 (C-5″), 131.8 (C-6″), 146.3 (C-7″), 115.1 (C-8″), 169.1 (C-9″), 101.5 (C-1‴), 72.2 (C-2‴), 72.3 (C-3‴), 73.1 (C-4‴), 69.3 (C-5‴), 17.3 (C-6‴)。综合上述理化常数及波谱数据,确定该化合物为文献[5]报道的 osmanthuside B_6。

化合物 **3** 无色粉末(甲醇),mp 135 ~ 137 ℃。ESI-MS *m/z* 447.5 [M + H]$^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.25 (1H, d, *J* = 7.8 Hz, H-1), 3.02 (1H, m, H-2), 3.16 (1H, m, H-3), 3.20 (1H, m, H-4), 3.43 (1H, m, H-5), 4.20 (1H, m, H_a-6), 4.44 (1H, m, H_b-6), 7.50 (2H, d, *J* = 8.6 Hz, H-2′, H-6′), 6.79 (2H, d, *J* = 8.6 Hz, H-3′, H-5′), 7.54 (1H, d, *J* = 15.9 Hz, H-7′), 6.40 (1H, d, *J* = 15.9 Hz, H-8′), 7.01 (2H, d, *J* = 8.4 Hz, H-2″, H-6″), 6.61 (2H, d, *J* = 8.4 Hz, H-3″, H-5″), 2.73 (2H, t, *J* = 7.4, 14.8 Hz, H-7″), 3.61 (1H, m, H_a-8″), 3.81 (1H, m, H_b-8″); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 104.2 (C-1), 74.9 (C-2), 77.6 (C-3), 71.5 (C-4), 75.1 (C-5), 64.6 (C-6), 126.8 (C-1′), 131.1 (C-2′), 116.4 (C-3′), 161.3 (C-4′), 116.4 (C-5′), 131.1 (C-6′), 146.6 (C-7′), 114.1 (C-8′), 168.1 (C-9′), 130.6 (C-1″), 130.5 (C-2″), 115.9 (C-3″), 156.8 (C-4″), 115.9 (C-5″), 130.5 (C-6″), 36.3 (C-7″), 72.2 (C-8″)。以上数据与文献[6]报道的 eutigoide A 的数据一致,故鉴定化合物 **3** 为 eutigoide A。

化合物 **4** 无色粉末(甲醇),mp 191 ~ 193 ℃。ESI-MS *m/z* 637.6 [M + H]$^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.29 (1H, d, *J* = 7.9 Hz, H-1), 3.52 (1H, m, H-2), 3.88 (1H, m, H-3), 3.28 (1H, m, H-4), 3.52 (1H, m, H-5), 4.25 (1H, m, H_a-6), 4.37 (1H, m, H_b-6), 7.32 (1H, d, *J* = 1.8 Hz, H-2′), 6.81 (1H, d, *J* = 8.1 Hz, H-5′), 7.08 (1H, dd, *J* = 1.8, 8.1 Hz, H-6′), 7.55 (1H, d, *J* = 15.8 Hz, H-7′), 6.52 (1H, d, *J* = 15.8 Hz, H-8′), 6.69 (1H, s, H-2″), 6.67 (1H, s, H-5″), 6.57 (1H, dd, *J* = 2.0, 8.2 Hz, H-6″), 2.70 (2H, m, H-7″), 3.62 (1H, m, H_a-8″), 3.92 (1H, m, H_b-8″), 5.05 (1H, s, H-1‴), 3.61 (1H, m, H-2‴), 3.71 (1H, m, H-3‴), 3.25 (1H, m, H-4‴), 3.92 (1H, m, H-5‴), 1.10 (3H, d, *J* = 6.2 Hz, H-6‴), 3.81 (3H, s, C3′-OCH_3)。^{13}C-NMR (125 MHz, DMSO-d_6) δ: 104.1 (C-1), 74.4 (C-2), 84.6 (C-3), 70.5 (C-4), 74.8 (C-5), 64.6 (C-6), 127.6 (C-1′), 111.8 (C-2′), 149.4 (C-3′), 148.9 (C-4′), 116.4 (C-5′), 124.0 (C-6′), 146.3 (C-7′), 115.1 (C-8′), 169.1 (C-9′), 130.2 (C-1″), 116.5 (C-2″), 143.9 (C-3″), 145.8 (C-4″), 115.1 (C-5″), 121.2 (C-6″), 36.3 (C-7″), 72.1 (C-8″), 101.5 (C-1‴), 72.2 (C-2‴), 71.8 (C-3‴), 74.1 (C-4‴), 70.3 (C-5‴), 18.1 (C-6‴), 56.1 (C3′-OCH_3)。根据以上理化常数及波谱数据,鉴定化合物 **4** 为文献[7]报道的 plantainoside C。

化合物 **5** 黄色粉末(甲醇),mp 139 ~ 140 ℃。ESI-MS *m/z* 479.4 [M + H]$^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.25 (1H, d, *J* = 7.9 Hz, H-1), 3.12 (1H, m, H-2), 3.16 (1H, m, H-3), 3.02 (1H, m, H-4), 3.43 (1H, m, H-5), 4.12 (1H, m, H_a-6), 4.44 (1H, m, H_b-6), 7.07 (1H, d, *J* = 2.1 Hz, H-2′), 6.76 (1H, d, *J* = 8.1 Hz, H-5′), 6.97 (1H, dd, *J* = 2.1, 8.1 Hz, H-6′), 7.48 (1H, d, *J* = 15.8 Hz, H-7′), 6.29 (1H, d, *J* = 15.8 Hz, H-8′), 6.61 (1H, d, *J* = 2.1 Hz, H-2″), 6.58 (1H, d, *J* = 7.9 Hz, H-5″), 6.46 (1H, dd, *J* = 2.1, 8.0 Hz, H-6″), 2.67 (2H, m, H-7″), 3.62 (1H, m, H_a-8″), 3.82 (1H, m, H_b-8″); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 105.5 (C-1),

73.2 (C-2), 76.5 (C-3), 70.5 (C-4), 74.2 (C-5), 67.6 (C-6), 125.9 (C-1′), 116.2 (C-2′), 145.4 (C-3′), 148.3 (C-4′), 115.3 (C-5′), 121.8 (C-6′), 145.1 (C-7′), 114.3 (C-8′), 168.3 (C-9′), 129.2 (C-1″), 116.5 (C-2″), 143.9 (C-3″), 145.8 (C-4″), 115.8 (C-5″), 119.4 (C-6″), 35.1 (C-7″), 70.6 (C-8″)。以上理化常数及波谱数据与文献[8]报道的 calceorioside B 完全一致,故鉴定化合物 **5** 为 calceorioside B。

化合物 **6** 黄色粉末(甲醇),mp 201 ~ 202 ℃。ESI-MS *m/z* 651.7 $[M+H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.29 (1H, d, *J* = 7.9 Hz, H-1), 3.52 (1H, m, H-2), 3.88 (1H, m, H-3), 3.28 (1H, m, H-4), 3.52 (1H, m, H-5), 4.25 (1H, m, H_a-6), 4.37 (1H, m, H_b-6), 7.32 (1H, d, *J* = 1.8 Hz, H-2′), 6.81 (1H, d, *J* = 8.1 Hz, H-5′), 7.08 (1H, dd, *J* = 1.8, 8.1 Hz, H-6′), 7.60 (1H, d, *J* = 15.8 Hz, H-7′), 6.49 (1H, d, *J* = 15.8 Hz, H-8′), 6.69 (1H, dd, *J* = 2.0 Hz, H-2″), 6.77 (1H, dd, *J* = 8.2 Hz, H-5″), 6.59 (1H, dd, *J* = 2.0, 8.2 Hz, H-6″), 2.70 (2H, m, H-7″), 3.62 (1H, m, H_a-8″), 3.92 (1H, m, H_b-8″), 5.07 (1H, s, H-1‴), 3.61 (1H, m, H-2‴), 3.71 (1H, m, H-3‴), 3.25 (1H, m, H-4‴), 3.92 (1H, m, H-5‴), 1.10 (3H, d, *J* = 6.2 Hz, H-6‴), 3.81 (3H, s, C3′-OCH_3), 3.70 (3H, s, C4″-OCH_3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 104.3 (C-1), 74.4 (C-2), 84.6 (C-3), 70.5 (C-4), 75.1 (C-5), 65.6 (C-6), 127.6 (C-1′), 111.3 (C-2′), 149.1 (C-3′), 149.9 (C-4′), 116.4 (C-5′), 123.0 (C-6′), 146.3 (C-7′), 115.1 (C-8′), 168.1 (C-9′), 130.2 (C-1″), 112.1 (C-2″), 146.9 (C-3″), 145.3 (C-4″), 115.1 (C-5″), 121.2 (C-6″), 36.3 (C-7″), 72.1 (C-8″), 102.1 (C-1‴), 72.0 (C-2‴), 71.8 (C-3‴), 74.3 (C-4‴), 70.3 (C-5‴), 18.1 (C-6‴), 56.5 (C3′-OCH_3), 56.4 (C4″-OCH_3)。综合以上波谱数据及化合物的理化常数,鉴定化合物 **6** 为文献[9]报道的 isomartynoside。

化合物 **7** 无色粉末(甲醇),mp 199 ~ 201 ℃。ESI-MS *m/z* 625.2 $[M+H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.37 (1H, d, *J* = 7.8 Hz, H-1), 3.55 (1H, m, H-2), 3.81 (1H, t, *J* = 9.2, 18.4 Hz, H-3), 4.96 (1H, d, *J* = 9.4 Hz, H-4), 3.40 (1H, m, H-5), 3.52 (1H, m, H_a-6), 3.63 (1H, m, H_b-6), 7.05 (1H, d, *J* = 1.8 Hz, H-2′), 6.78 (1H, d, *J* = 8.2 Hz, H-5′), 6.95 (1H, dd, *J* = 1.8, 8.2 Hz, H-6′), 7.59 (1H, d, *J* = 15.9 Hz, H-7′), 6.28 (1H, d, *J* = 15.9 Hz, H-8′), 6.70 (1H, d, *J* = 1.8 Hz, H-2″), 6.56 (1H, d, *J* = 8.0 Hz, H-5″), 6.68 (1H, dd, *J* = 1.8, 8.0 Hz, H-6″), 2.79 (2H, m, H-7″), 3.92 (1H, m, H_a-8″), 4.04 (1H, m, H_b-8″), 5.19 (1H, d, *J* = 7.8 Hz, H-1‴), 3.58 (1H, m, H-2‴), 3.60 (1H, m, H-3‴), 3.30 (1H, m, H-4‴), 3.92 (1H, m, H-5‴), 1.09 (3H, d, *J* = 6.1 Hz, H-6‴); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 104.5 (C-1), 76.5 (C-2), 83.5 (C-3), 70.2 (C-4), 76.2 (C-5), 62.6 (C-6), 127.6 (C-1′), 115.2 (C-2′), 146.7 (C-3′), 149.7 (C-4′), 116.5 (C-5′), 123.1 (C-6′), 148.1 (C-7′), 114.3 (C-8′), 168.3 (C-9′), 131.5 (C-1″), 117.1 (C-2″), 144.6 (C-3″), 146.8 (C-4″), 116.8 (C-5″), 121.4 (C-6″), 36.5 (C-7″), 72.3 (C-8″), 102.5 (C-1‴), 70.7 (C-2‴), 72.0 (C-3‴), 73.3 (C-4‴), 70.3 (C-5‴), 18.4 (C-6‴)。以上化合物 **7** 的理化常数及波谱数据与文献[10]报道的 verbascoside 的理化常数及波谱数据完全一致,故鉴定化合物 **7** 为 verbascoside。

化合物 **8** 无色粉末(甲醇),mp 191 ~ 193 ℃。ESI-MS *m/z* 625.6 $[M+H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.32 (1H, d, *J* = 7.4 Hz, H-1), 3.60 (1H, m, H-2), 3.11 (1H, m, 18.4 Hz, H-3), 4.65 (1H, t, *J* = 9.5, 18.9 Hz, H-4), 3.46 (1H, m, H-5), 3.35 (1H, m, H_a-6), 3.54 (1H, m, H_b-6), 7.00 (1H, s, H-2′), 6.77 (1H, s, H-5′), 7.05 (1H, d, *J* = 7.8 Hz, H-6′), 7.50 (1H, d, *J* = 16.0 Hz, H-7′), 6.26 (1H, d, *J* = 16.0 Hz, H-8′), 6.64 (1H, s, H-2″), 6.50 (1H, s, H-5″), 6.63 (1H, d, *J* = 7.5 Hz, H-6″), 2.70 (2H, m, H-7″), 3.60 (1H, m, H_a-8″), 3.84 (1H, m, H_b-8″), 4.53 (1H, m, H-1‴), 3.48 (1H, m, H-2‴), 3.46 (1H, m, H-3‴), 3.16 (1H, m, H-4‴), 3.38 (1H, m, H-5‴), 1.05 (3H, d, *J* = 5.5 Hz, H-6‴); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 102.5 (C-1), 72.5 (C-2), 73.5 (C-3), 71.2 (C-4), 73.2 (C-5), 66.6 (C-6), 125.6 (C-1′), 115.2 (C-2′), 145.7 (C-3′), 148.7 (C-4′), 114.5 (C-5′), 121.1 (C-6′), 145.1 (C-7′), 113.3 (C-8′), 165.3 (C-9′), 129.5 (C-1″), 116.1 (C-2″), 144.6 (C-3″), 143.8 (C-4″), 115.8 (C-5″), 119.4 (C-6″), 35.5 (C-7″), 70.3 (C-8″), 100.5 (C-1‴), 70.7 (C-2‴), 73.0 (C-3‴), 71.3 (C-4‴), 68.3 (C-5‴), 17.4 (C-

6‴)。以上数据与文献[11]报道的 acteoside 的数据一致,故鉴定化合物 **8** 为 acteoside。

化合物 **9** 无色粉末(甲醇),mp 145 ~ 147 ℃。ESI-MS *m/z* 479.5 $[M+H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.29 (1H, d, J = 7.8 Hz, H-1), 3.10 (1H, m, H-2), 3.45 (1H, m, H-3), 4.64 (1H, t, J = 9.5, 19.0 Hz, H-4), 3.32 (1H, m, H-5), 3.40 (2H, m, H-6), 7.06 (1H, s, H-2′), 6.76 (1H, d, J = 8.1 Hz, H-5′), 6.97 (1H, dd, J = 1.6, 8.1 Hz, H-6′), 7.47 (1H, d, J = 15.2 Hz, H-7′), 6.23 (1H, d, J = 15.2 Hz, H-8′), 6.63 (1H, d, J = 2.0 Hz, H-2″), 6.64 (1H, d, J = 8.0 Hz, H-5″), 6.49 (1H, dd, J = 2.0, 8.0 Hz, H-6″), 2.70 (2H, m, H-7″), 3.58 (1H, m, H_a-8″), 3.88 (1H, m, H_b-8″); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 101.5 (C-1), 72.5 (C-2), 71.7 (C-3), 70.5 (C-4), 73.2 (C-5), 62.5 (C-6), 126.9 (C-1′), 114.0 (C-2′), 147.7 (C-3′), 145.6 (C-4′), 116.3 (C-5′), 123.1 (C-6′), 147.1 (C-7′), 115.3 (C-8′), 168.1 (C-9′), 130.2 (C-1″), 116.8 (C-2″), 142.9 (C-3″), 145.7 (C-4″), 117.8 (C-5″), 121.2 (C-6″), 36.7 (C-7″), 72.2 (C-8″)。根据以上波谱数据及理化常数,确定化合物 **9** 为文献[12]报道的 desrhamnosyl acteoside。

化合物 **10** 黄色粉末(甲醇),mp 263 ~ 264 ℃。ESI-MS *m/z* 477.4 $[M+H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 6.91 (1H, s, H-3), 6.68 (1H, s, H-6), 7.28 (1H, d, J = 8.1 Hz, H-3′), 7.61 (1H, m, H-4′), 7.21 (1H, m, H-5′), 7.89 (1H, dd, J = 1.7, 7.8 Hz, H-6′), 5.06 (1H, d, J = 7.5 Hz, H-1″), 3.22 (1H, m, H-2″), 3.23 (1H, m, H-3″), 3.17 (1H, m, H-4″), 3.45 (1H, m, H-5″), 3.48 (1H, m, H_a-6″), 3.71 (1H, br d, J = 11.1 Hz, H_b-6″), 3.85 (3H, s, C8-OCH_3), 3.94 (3H, s, C2′-OCH_3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 162.2 (C-2), 110.1 (C-3), 182.7 (C-4), 156.9 (C-5), 99.1 (C-6), 156.4 (C-7), 129.5 (C-8), 149.7 (C-9), 105.4 (C-10), 119.9 (C-1′), 158.3 (C-2′), 113.1 (C-3′), 133.8 (C-4′), 121.4 (C-5′), 129.5 (C-6′), 100.7 (C-1″), 73.6 (C-2″), 77.0 (C-3″), 70.0 (C-4″), 77.6 (C-5″), 61.0 (C-6″), 56.8 (C8-OCH_3), 61.8 (C2′-OCH_3)。以上数据与文献[13]报道的 5,7-二羟基-8,2′-二甲氧基-7-*O*-*β*-*D*-葡萄糖苷的数据一致,故鉴定化合物 **10** 为 5,7-二羟基-8,2′-二甲氧基-7-*O*-*β*-*D*-葡萄糖苷。

化合物 **11** 黄色粉末(甲醇),mp 266 ~ 267 ℃。ESI-MS *m/z* 416.4 $[M+H]^+$。^{1}H-NMR (500 MHz, DMSO-d_6) δ: 6.88 (1H, s, H-3), 6.47 (1H, d, J = 2.1 Hz, H-6), 6.86 (1H, d, J = 2.1 Hz, H-8), 7.95 (2H, d, J = 8.8 Hz, H-2′, H-6′), 6.96 (2H, d, J = 8.8 Hz, H-3′, H-5′), 5.31 (1H, d, J = 7.5 Hz, H-1″), 3.43 (1H, m, H-2″), 5.49 (1H, m, H-3″), 3.25 (1H, m, H-4″), 4.05 (1H, m, H-5″), 1.03 (3H, d, J = 6.2 Hz, H-6″); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 162.8 (C-2), 103.5 (C-3), 182.4 (C-4), 161.9 (C-5), 99.6 (C-6), 164.8 (C-7), 95.1 (C-8), 157.4 (C-9), 105.9 (C-10), 121.3 (C-1′), 129.0 (C-2′), 121.3 (C-3′), 161.6 (C-4′), 121.3 (C-5′), 129.0 (C-6′), 99.7 (C-1″), 73.2 (C-2″), 75.6 (C-3″), 71.6 (C-4″), 76.0 (C-5″), 18.9 (C-6″)。综合以上波谱数据及化合物的理化常数,鉴定化合物 **11** 为文献[14]报道的洋芹素-7-*O*-鼠李糖苷。

4 讨论

本文对国产盔状黄芩中的苷类化合物进行了较系统的研究,共发现 11 个苷类化合物,包括 9 个苯乙醇苷和 2 个黄酮苷。其中 7 个苯乙醇苷(化合物 **1** ~ **4**, **7** ~ **9**),2 个黄酮苷(化合物 **10**, **11**)为首次从该植物中发现。

Toshio 等[7]和 El-Emary 等[15]研究人员曾对实验中发现的 plantainoside C,洋芹素-7-*O*-鼠李糖苷等化合物的生物活性进行研究,证明其具有显著的抗氧化、抗炎活性,与盔状黄芩清热解毒的功效相一致。本研究对盔状黄芩的药效物质基础进行了初步探明,为该植物的进一步开发提供了科学依据。

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