·基础研究·

膜荚黄芪叶中三萜皂苷类成分的分离与鉴定△

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［摘要］ **目的：**研究膜荚黄芪叶中的三萜皂苷类成分。**方法：**采用硅胶、十八烷基硅烷键合硅胶（ODS）等色谱方法对膜荚黄芪叶的化学成分进行分离，通过一维核磁共振氢谱（^{1}D-NMR）和 ^{2}D-NMR 法分析鉴定化合物。**结果：**从膜荚黄芪叶提取物中共分离出 15 个化合物，分别鉴定为黄芪叶苷 B（**1**）、黄芪叶苷 L（**2**）、cyclounifolioside D（**3**）、3-*O*-[α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃木糖基]-6-*O*-β-*D*-吡喃葡萄糖基-24-*O*-α-*L*-吡喃阿拉伯糖基-16-乙酰基-3β,6α,16β,24(*S*),25-五羟基环菠萝蜜烷（**4**）、黄芪叶苷 K（**5**）、黄芪叶苷 A（**6**）、astraverrucin Ⅰ（**7**）、cycloaraloside A（**8**）、黄芪叶苷 D（**9**）、astralanosaponin D（**10**）、大豆皂醇 E（**11**）、3β,21α,24-三羟基-齐墩果-12-烯（**12**）、3β,22β,24,29-四羟基齐墩果-12-烯（**13**）、豌豆皂苷Ⅰ（**14**）、大豆皂醇 B-3-*O*-β-*D*-吡喃葡萄糖醛酸基-(1→2)-β-*D*-吡喃葡萄糖基-(1→4)-α-*L*-吡喃鼠李糖苷（**15**）。**结论：**化合物 **3**、**4**、**7**、**8** 为首次从膜荚黄芪中分离得到，化合物 **11**~**15** 为首次从黄芪属植物中分离得到。

［关键词］ 黄芪叶；三萜皂苷；化学成分

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Isolation and Identification of Triterpenoid Saponins from Leaves of *Astragalus membranaceus*

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[**Abstract**] **Objective**: To study triterpenoid saponins in the leaves of *Astragalus membranaceus*. **Methods**: The chemical constituents in leaves of *A. membranaceus* were isolated by silica gel and ODS chromatography, and the compounds were identified by ^{1}D-NMR and ^{2}D-NMR. **Results**: Fifteen compounds were isolated and identified from the extract of *A. membranaceus* leaves, which were huangqiyenin B (**1**), huangqiyenin L (**2**) and cyclounifolioside D (**3**), 3-*O*-[α-*L*-rhamnopyranosyl-(1→2)-β-*D*-xylopyranosyl]-6-*O*-β-*D*-glucopyranosyl-24-*O*-α-*L*-arabinopyranosyl-16-*O*-acetoxy-3β,6α,16β,24(*S*),25-pentahydroxycycloartane (**4**), huangqiyenin K (**5**), huangqiyenin A (**6**), astraverrucin Ⅰ (**7**), cycloaraloside A (**8**), huangqiyenin D (**9**), astralanosaponin D (**10**), soyasapogenol E (**11**), 3β,21α,24-trihydroxy-oleantho-12-ene (**12**), 3β,22β,24,29-tetrahydroxy oleantho-12-ene (**13**), pisumsaponins Ⅰ (**14**), and soyasapogenol B-3-*O*-β-*D*-glucopyranosyl-(1→2)-β-*D*-glucopyranoside-(1→4)-α-*L*-rhamnopyranosyl (**15**). **Conclusion**: Compounds **3**, **4**, **7**, and **8** were isolated from leaves of *A. membranaceus* for the first time and **11**-**15** were isolated from the genus *Astragalus* for the first time.

[**Keywords**] leaves of *Astragalus membranaceus* (Fish.) Bge. ; triterpenoids; chemical composition

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膜荚黄芪 *Astragalus membranaceus*（Fish.）Bge. 属于豆科（Leguminosae）黄芪属（*Astragalus* Linn.）多年生草本植物，始载于《神农本草经》，具有补气固表、托毒排脓、利尿、生肌的功效[1]。《中药大辞典》对黄芪茎叶的描述引自《名医别录》，其记录黄芪茎叶具有“疗渴及筋挛，痈肿，疽疮”的作用[2]。《中华人民共和国药典》2020年版规定黄芪的来源为豆科植物蒙古黄芪 *A. membranaceus*（Fisch.）Bge. var. *mongholicus*（Bge.）Hsiao或膜荚黄芪 *A. membranaceus*（Fisch.）Bge. 的干燥根[3]。随着黄芪临床应用的增加，野生黄芪数量急剧减少，国内外学者开始对黄芪的地上部分进行研究，并从中分离得到多种化学成分，其主要的化学成分包括黄酮类[4]、皂苷类[5]及少量的多糖[6]。王知斌等[7]从膜荚黄芪叶中分离得到了13个黄酮类化合物，其中有3个化合物首次从黄芪属中分离得到。本研究对膜荚黄芪叶的化学成分进行研究，共分离得到15个三萜皂苷类化合物，包括10个环菠萝蜜烷型三萜皂苷和5个齐墩果烷型三萜皂苷，为膜荚黄芪叶的进一步研究提供参考。

1　材料

1.1　仪器与耗材

2695型分析型高效液相色谱仪（美国Waters公司）；LC-6AD型制备型高效液相色谱仪、RID型示差折光检测器（日本岛津公司）；QTOF™ 5600$^+$型质谱仪（美国AB Sciex公司）；DPX-600型超导核磁共振波谱仪、DPX-400型超导核磁共振波谱仪（瑞士Bruker公司）；分析型Sunfire™ C_{18}色谱柱（150 mm×4.6 mm，5 μm）、半制备型Sunfire Prep™ C_{18}色谱柱（250 mm×10 mm，10 μm）、制备型Sunfire Prep™ C_{18}色谱柱（250 mm×19 mm，10 μm）；正相柱色谱用硅胶（200~300、80~100目，青岛海洋化工厂）；A-HG型反相柱色谱用十八烷基硅烷键合硅胶（ODS，50 μm，日本YMC公司）；Silicagel60 F_{254}薄层色谱硅胶板（德国Merck公司）；Sephadex LH-20（美国Pharmacia公司）。

1.2　试药

膜荚黄芪叶于2017年8月在黑龙江省大兴安岭地区采集，经黑龙江中医药大学药用植物教研室樊锐锋副教授鉴定为豆科黄芪属植物膜荚黄芪 *Astragalus membranaceus*（Fish.）Bge. 的叶。标本现保存于黑龙江中医药大学药学院（标本号：2017W101）；甲醇（色谱纯，北京百灵威科技有限公司）；甲醇（分析纯，西陇科学股份有限公司）。

2　提取与分离

取膜荚黄芪干燥叶10.0 kg，以15倍量75%乙醇加热回流提取3次，每次2 h，滤过，合并提取液。提取液减压回收溶剂，得浸膏1 395.0 g，计算其出膏率为14.0%。浸膏加水6 L混悬溶解，依次用石油醚（6 L×3次）、乙酸乙酯（6 L×3次）、水饱和正丁醇（6 L×3次）萃取，分别减压回收溶剂得石油醚萃取物50.0 g、乙酸乙酯萃取物190.0 g、正丁醇萃取物195.0 g。正丁醇萃取物经正相硅胶柱色谱分离，以二氯甲烷-甲醇（20∶1→10∶1→5∶1→3∶1→2∶1→1∶1）梯度洗脱，合并相同流分得Fr. 1~Fr. 11。Fr. 1（13.0 g）经反相ODS柱色谱分离，以甲醇洗脱，分离得到化合物**11**（5.3 mg）、**12**（6.8 mg）和**13**（7.1 mg）。Fr. 2（26.9 g）经反相ODS柱色谱分离，50%~90%甲醇梯度洗脱，合并相同流分得Fr. 2.1~Fr. 2.15。Fr. 2.11经半制备型高效液相色谱法（HPLC）分离，以甲醇-水（80∶20）洗脱，得到化合物**5**（168.2 mg，t_R=30.8 min）。Fr. 3（17.6 g）经反相ODS柱色谱分离，10%~90%甲醇梯度洗脱，合并相同流分得Fr. 3.1~Fr. 3.10。Fr. 3.6进一步经制备型HPLC分离，以甲醇-水（20∶80）洗脱，分离得到化合物**14**（11.5 mg，t_R=24.9 min）和**15**（8.3 mg，t_R=28.3 min）。Fr. 4（9.0 g）经反相ODS柱色谱分离，60%~90%甲醇梯度洗脱，合并相同流分得Fr. 4.1~Fr. 4.8，Fr. 4.3经半制备型HPLC分离，以甲醇-水（80∶20）洗脱，分离得到化合物**3**（12.7 mg，t_R=27.0 min）和**9**（30.0 mg，t_R=31.1 min）。

Fr. 5（12.3 g）经反相ODS柱色谱分离，50%~80%甲醇洗脱，合并相同流分得Fr. 5.1~Fr. 5.13。Fr. 5.10经制备型HPLC分离，以甲醇-水（65∶35）洗脱，得到化合物**6**（364.2 mg，t_R=27.5 min）。Fr. 6（21.9 g）经反相ODS柱色谱分离，40%~70%甲醇梯度洗脱，合并相同组分得到Fr. 6.1~Fr. 6.10。Fr. 6.5经制备型HPLC分离，以甲醇-水（65∶35）洗脱，得到化合物**1**（121.0 mg，t_R=28.0 min）。Fr. 6.9经制备型HPLC分离，以甲醇-水（75∶25）洗脱，得到化合物**4**（7.9 mg，t_R=23.2 min）；Fr. 7（12.4 g）经反相ODS柱色谱分离，40%~85%甲醇

梯度洗脱，合并相同组分得到Fr. 7. 1~7. 15。Fr. 7. 5经制备型HPLC分离，以甲醇-水（64∶36）洗脱，分离得到化合物**7**（187. 3 mg，t_R=28. 7 min）。Fr. 7. 11经制备型HPLC分离，以甲醇-水（80∶20）洗脱，得到化合物**10**（59. 2 mg，t_R=24. 0 min）和**8**（16. 2 mg，t_R=29. 2 min）。Fr. 9（29. 2 g）经反相ODS柱色谱分离，40%~70%甲醇梯度洗脱，得到Fr. 9. 1~Fr. 9. 11。Fr. 9. 7经制备型HPLC，以甲醇-水（55∶45）洗脱，分离得到化合物**2**（25. 6 mg，t_R=28. 0 min）。

3　结构鉴定

化合物**1**：白色无定形粉末；ESI-MS *m/z* 651 $[M-H]^-$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 67 (1H, br s, H-3), 4. 94 (1H, d, *J*=7. 6 Hz, H-1′), 4. 71 (1H, m, H-16), 4. 60 (1H, d, *J*=11. 5 Hz, H-6′), 4. 42 (1H, dd, *J*=11. 5, 5. 2 Hz, H-6′), 4. 24 (1H, m, H-3′), 4. 24 (1H, m, H-4′), 4. 05 (1H, m, H-2′), 3. 91 (2H, d, *J*=10. 9 Hz, H-5′), 3. 58 (1H, br s, H-24), 3. 50 (1H, d, *J*=11. 6, 7. 8 Hz, H-7), 2. 60 (1H, d, *J*=11. 6, 7. 8 Hz, H-7), 2. 47 (1H, br s, H-17), 2. 29 (2H, m, H-2), 2. 24 (1H, m, H-8), 2. 21 (1H, s, H-5), 2. 13 (2H, m, H-15), 1. 97 (1H, m, H-20), 1. 88 (2H, m, H-23), 1. 83 (3H, s, H-26), 1. 73 (2H, m, H-22), 1. 70 (2H, m, H-11), 1. 68 (2H, m, H-12), 1. 55 (2H, m, H-1), 1. 47 (3H, s, H-27), 1. 44 (3H, s, H-28), 1. 33 (3H, s, H-29), 1. 24 (3H, s, H-30), 1. 05 (3H, d, *J*=6. 1 Hz, H-21), 0. 94 (3H, s, H-18), 0. 66 (1H, d, *J*=4. 6 Hz, H-19b), 0. 07 (1H, d, *J*=4. 6 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 29. 0 (C-1), 30. 2 (C-2), 87. 8 (C-3), 41. 2 (C-4), 57. 7 (C-5), 211. 4 (C-6), 41. 5 (C-7), 42. 6 (C-8), 21. 6 (C-9), 29. 9 (C-10), 26. 6 (C-11), 33. 1 (C-12), 45. 7 (C-13), 47. 7 (C-14), 45. 9 (C-15), 71. 3 (C-16), 56. 5 (C-17), 18. 4 (C-18), 21. 6 (C-19), 28. 7 (C-20), 15. 6 (C-21), 32. 7 (C-22), 27. 8 (C-23), 77. 2 (C-24), 72. 4 (C-25), 25. 7 (C-26), 26. 3 (C-27), 18. 9 (C-28), 26. 9 (C-29), 15. 3 (C-30), 106. 8 (C-1′), 75. 7 (C-2′), 78. 6 (C-3′), 71. 7 (C-4′), 78. 2 (C-5′), 63. 0 (C-6′)。该化合物数据与文献[8]报道的数据基本一致，故鉴定化合物**1**为黄芪叶苷B。

化合物**2**：白色无定形粉末；ESI-MS *m/z* 811 $[M+H]^+$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 73 (1H, d, *J*=6. 0 Hz, H-24), 5. 00 (1H, m, H-6), 4. 95 (1H, d, *J*=7. 8 Hz, H-1″), 4. 89 (1H, d, *J*=7. 5 Hz, H-1′), 4. 57 (1H, m, H-16), 4. 57 (1H, d, *J*=11. 0 Hz, H-6″), 4. 44 (1H, dd, *J*=11. 0, 5. 0 Hz, H-6″), 4. 38 (1H, dd, *J*=11. 0, 5. 0 Hz, H-5′), 4. 25 (2H, s, H-26), 4. 22 (1H, m, H-4′), 4. 22 (1H, m, H-2″), 4. 22 (1H, m, H-3″), 4. 22 (1H, m, H-4″), 4. 06 (1H, m, H-3′), 4. 01 (1H, m, H-2′), 3. 95 (1H, m, H-5″), 3. 74 (1H, dd, *J*=11. 0, 10. 1 Hz, H-5′), 3. 55 (1H, m, H-3), 2. 17 (2H, m, H-23), 2. 27 (1H, m, H-20), 1. 97 (1H, m, H-8), 1. 96 (2H, m, H-2), 1. 86 (1H, d, H-5), 1. 80 (1H, m, H-17), 1. 78 (3H, s, H-27), 1. 70 (2H, m, H-15), 1. 63 (2H, m, H-12), 1. 53 (2H, m, H-7), 1. 44 (3H, s, H-29), 1. 32 (3H, s, H-18), 1. 25 (2H, m, H-11), 1. 24 (2H, m, H-22), 1. 21 (2H, m, H-1), 1. 18 (3H, s, H-28), 1. 04 (3H, d, *J*=6. 6 Hz, H-21), 0. 97 (3H, s, H-30), 0. 49 (1H, d, *J*=6. 0 Hz, H-19b), 0. 18 (1H, d, *J*=6. 6 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 31. 9 (C-1), 29. 8 (C-2), 87. 8 (C-3), 42. 1 (C-4), 50. 0 (C-5), 70. 7 (C-6), 33. 3 (C-7), 45. 4 (C-8), 20. 9 (C-9), 28. 2 (C-10), 25. 9 (C-11), 32. 9 (C-12), 45. 7 (C-13), 46. 6 (C-14), 48. 8 (C-15), 71. 0 (C-16), 56. 7 (C-17), 18. 6 (C-18), 28. 4 (C-19), 30. 6 (C-20), 18. 1 (C-21), 36. 5 (C-22), 25. 5 (C-23), 129. 4 (C-24), 131. 8 (C-25), 14. 1 (C-26), 75. 1 (C-27), 26. 9 (C-28), 16. 5 (C-29), 19. 9 (C-30), 21. 7 (6-CH_3CO), 170. 2 (6-CH_3CO), 106. 9 (C-1′), 75. 7 (C-2′), 78. 7 (C-3′), 71. 0 (C-4′), 62. 8 (C-5′), 103. 4 (C-1″), 75. 2 (C-2″), 78. 6 (C-3″), 71. 7 (C-4″), 78. 4 (C-5″), 62. 9 (C-6″)。该化合物数据与文献[9]报道的数据基本一致，故鉴定化合物**2**为黄芪叶苷L。

化合物**3**：白色无定形粉末；ESI-MS *m/z* 741 $[M+HCOO]^-$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 51 (1H, m, H-16), 4. 99 (1H, d, *J*=7. 5 Hz, H-1′), 4. 55 (1H, m, H-6′), 4. 42 (1H, m, H-6′), 4. 26 (1H, m, H-3′), 4. 24 (1H, m, H-4′), 4. 10 (1H, m, H-2′), 3. 96 (1H, m, H-6), 3. 95 (1H, m, H-3), 3. 95 (1H, m, H-5′), 3. 62 (1H, m, H-24), 2. 25 (1H, m, H-23b), 2. 12 (2H, m, H-15), 2. 07 (3H, s, 16-CH_3CO), 2. 06 (1H, m, H-22b), 2. 01 (3H, s, H-26), 1. 91 (1H, m, H-20), 1. 90 (1H, m, H-17), 1. 84 (1H, m, H-8), 1. 81 (1H, m, H-11b), 1. 74 (1H, m, H-5), 1. 64 (2H, m, H-7), 1. 64 (1H, m, H-12b), 1. 58 (2H, m, H-1), 1. 49 (2H, m, H-2),

1. 47 (1H, m, H-23a), 1. 39 (3H, s, H-27), 1. 38 (1H, m, H-12a), 1. 31 (3H, s, H-29), 1. 26 (1H, m, H-11a), 1. 25 (3H, s, H-18), 1. 25 (3H, s, H-30), 1. 08 (1H, m, H-22a), 1. 03 (3H, d, *J*=7. 0 Hz, H-21), 0. 98 (3H, s, H-28), 0. 56 (1H, d, *J*=4. 6 Hz, H-19b), 0. 30 (1H, d, *J*=4. 6 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 32. 7 (C-1), 30. 9 (C-2), 88. 4 (C-3), 42. 4 (C-4), 50. 5 (C-5), 70. 4 (C-6), 34. 0 (C-7), 46. 1 (C-8), 20. 4 (C-9), 29. 5 (C-10), 26. 4 (C-11), 33. 4 (C-12), 46. 2 (C-13), 46. 3 (C-14), 46. 1 (C-15), 75. 6 (C-16), 57. 1 (C-17), 18. 8 (C-18), 27. 8 (C-19), 31. 5 (C-20), 19. 1 (C-21), 32. 7 (C-22), 27. 8 (C-23), 79. 0 (C-24), 72. 0 (C-25), 26. 4 (C-26), 26. 4 (C-27), 19. 2 (C-28), 29. 6 (C-29), 16. 4 (C-30), 104. 0 (C-1′), 75. 6 (C-2′), 78. 9 (C-3′), 71. 7 (C-4′), 77. 7 (C-5′), 63. 1 (C-6′)。该化合物数据与文献[10]报道的数据基本一致，故鉴定化合物 **3** 为 cyclounifolioside D。

化合物 **4**：白色无定形粉末；ESI-MS *m*/*z* 1129 $[M+Na]^+$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 08 (1H, d, *J*=7. 9 Hz, H-16), 5. 08 (1H, d, *J*=1. 9 Hz, H-1′), 4. 97 (1H, d, *J*=7. 8 Hz, H-1‴), 4. 87 (2H, m, H-5⁗), 4. 62 (1H, m, H-4⁗), 4. 45 (2H, m, H-6‴), 4. 42 (1H, d, *J*=7. 6 Hz, H-1″), 4. 41 (1H, m, H-2‴), 4. 41 (1H, m, H-3‴), 4. 33 (1H, d, *J*=7. 1 Hz, H-1⁗), 4. 24 (1H, m, H-2‴), 4. 24 (1H, m, H-3‴), 4. 08 (1H, m, H-5′), 4. 08 (1H, m, H-5‴), 3. 96 (1H, m, H-2′), 3. 96 (1H, m, H-4‴), 3. 94 (2H, m, H-5″), 3. 79 (1H, m, H-3′), 3. 62 (1H, m, H-24), 3. 57 (1H, m, H-6), 3. 57 (1H, m, H-2″), 3. 57 (1H, m, H-3″), 3. 55 (1H, m, H-4′), 3. 55 (1H, m, H-4″), 3. 21 (1H, m, H-3), 2. 45 (1H, dd, *J*=16. 0, 6. 2 Hz, H-15), 2. 05 (3H, s, 16-CH_3CO), 2. 03 (1H, m, H-22a), 2. 00 (1H, m, H-8), 1. 99 (1H, m, H-2b), 1. 92 (1H, m, H-17), 1. 89 (1H, m, H-11b), 1. 84 (1H, m, H-7b), 1. 82 (2H, m, H-12), 1. 80 (1H, m, H-23b), 1. 77 (1H, m, H-7a), 1. 70 (1H, m, H-2a), 1. 62 (1H, m, H-5), 1. 59 (1H, m, H-1b), 1. 45 (3H, s, H-28), 1. 43 (3H, s, H-27), 1. 34 (3H, s, H-26), 1. 32 (1H, m, H-11a), 1. 31 (1H, m, H-1a), 1. 31 (1H, dd, *J*=16. 0, 8. 4 Hz, H-15), 1. 26 (3H, d, *J*=3. 2 Hz, H-6′), 1. 16 (3H, s, H-18), 1. 15 (1H, m, H-23a), 1. 07 (3H, s, H-30), 1. 05 (3H, d, *J*=6. 4 Hz, H-21), 0. 99 (1H, m, H-22b), 0. 97 (3H, s, H-29), 0. 51 (1H, d, *J*=4. 1 Hz, H-19b), 0. 18 (1H, d, *J*=4. 1 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 32. 7 (C-1), 30. 4 (C-2), 88. 3 (C-3), 42. 6 (C-4), 50. 4 (C-5), 79. 2 (C-6), 33. 5 (C-7), 45. 7 (C-8), 21. 4 (C-9), 29. 7 (C-10), 26. 4 (C-11), 33. 6 (C-12), 46. 2 (C-13), 47. 1 (C-14), 46. 2 (C-15), 76. 1 (C-16), 57. 6 (C-17), 18. 1 (C-18), 27. 3 (C-19), 33. 6 (C-20), 18. 9 (C-21), 33. 7 (C-22), 29. 7 (C-23), 90. 7 (C-24), 75. 6 (C-25), 25. 3 (C-26), 22. 1 (C-27), 28. 5 (C-28), 16. 9 (C-29), 20. 3 (C-30), 108. 1 (C-1′), 78. 7 (C-2′), 78. 7 (C-3′), 71. 35 (C-4′), 67. 3 (C-5′), 105. 9 (C-1″), 72. 0 (C-2″), 71. 6 (C-3″), 72. 9 (C-4″), 71. 1 (C-5″), 19. 0 (C-6″), 106. 3 (C-1‴), 75. 8 (C-2‴), 78. 8 (C-3‴), 71. 6 (C-4‴), 78. 9 (C-5‴), 62. 9 (C-6‴), 107. 3 (C-1⁗), 72. 9 (C-2⁗), 72. 8 (C-3⁗), 69. 9 (C-4⁗), 63. 4 (C-5⁗)。该化合物数据与文献[11]报道的数据基本一致，故鉴定化合物 **4** 为 3-*O*-[*α*-*L*-吡喃鼠李糖基-(1→2)-*β*-*D*-吡喃木糖基]-6-*O*-*β*-*D*-吡喃葡萄糖基-24-*O*-*α*-*L*-吡喃阿拉伯糖基-16-乙酰基-3*β*,6*α*,16*β*,24(*S*),25-五羟基环菠萝蜜烷。

化合物 **5**：白色无定形粉末；ESI-MS *m*/*z* 665 $[M+H]^+$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 00 (1H, m, H-6), 4. 85 (1H, d, *J*=7. 5 Hz, H-1′), 4. 73 (1H, dd, *J*=12. 5, 6. 9 Hz, H-16), 4. 38 (1H, dd, *J*=11. 0, 5. 0 Hz, H-5′b), 4. 23 (1H, m, H-4′), 4. 16 (1H, m, H-3′), 4. 10 (1H, dd, *J*=10. 6, 5. 7 Hz, H-24), 4. 03 (1H, m, H-2′), 3. 77 (1H, dd, *J*=11. 0, 10. 1 Hz, H-5′a), 3. 53 (1H, dd, *J*=11. 3, 3. 3 Hz, H-3), 2. 62 (1H, m, H-22b), 2. 39 (1H, m, H-2b), 2. 28 (1H, d, *J*=7. 7 Hz, H-17), 2. 15 (1H, m, H-23b), 2. 14 (1H, m, H-11b), 2. 08 (1H, m, H-15b), 2. 05 (3H, s, 6-CH_3CO), 1. 99 (1H, dd, *J*=10. 7, 6. 2 Hz, H-8), 1. 97 (1H, m, H-2a), 1. 90 (1H, m, H-23a), 1. 86 (1H, m, H-11a), 1. 84 (1H, m, H-22a), 1. 82 (1H, d, *J*=9. 3 Hz, H-5), 1. 78 (1H, m, H-15a), 1. 75 (1H, m, H-7b), 1. 75 (1H, m, H-12b), 1. 65 (1H, m, H-1b), 1. 51 (3H, s, H-18), 1. 44 (1H, m, H-7a), 1. 44 (1H, m, H-12a), 1. 42 (3H, d, *J*=5. 1 Hz, H-21), 1. 41 (3H, s, H-27), 1. 39 (3H, s, H-29), 1. 29 (3H, s, H-26), 1. 24 (1H, m, H-1a), 1. 17 (3H, s, H-28), 0. 98 (3H, s, H-30), 0. 54 (1H, d, *J*=4. 0 Hz, H-19b), 0. 25 (1H, d, *J*=4. 0 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 32. 3 (C-1), 30. 2 (C-2), 87. 7 (C-3), 42. 5 (C-4), 50. 4 (C-5), 70. 9 (C-6), 33. 5 (C-7), 45. 6 (C-8), 21. 0 (C-9), 28. 7 (C-10), 25. 7 (C-11), 33. 6 (C-12), 46. 6 (C-13), 46. 9 (C-

14), 49. 0 (C-15), 73. 1 (C-16), 56. 8 (C-17), 21. 0 (C-18), 29. 2 (C-19), 87. 7 (C-20), 29. 5 (C-21), 38. 6 (C-22), 26. 3 (C-23), 87. 9 (C-24), 70. 4 (C-25), 26. 5 (C-26), 27. 4 (C-27), 27. 2 (C-28), 16. 7 (C-29), 20. 3 (C-30), 107. 9 (C-1′), 75. 7 (C-2′), 78. 9 (C-3′), 71. 4 (C-4′), 67. 4 (C-5′)。该化合物数据与文献[10]报道的数据基本一致，故鉴定化合物**5**为黄芪叶苷K。

化合物**6**：白色无定形粉末；ESI-MS *m/z* 651 $[M+H]^+$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 78 (1H, br s, H-3), 5. 04 (1H, m, H-16), 4. 96 (1H, d, *J*=7. 7 Hz, H-1′), 4. 95 (1H, m, H-6′b), 4. 62 (1H, m, H-6′a), 4. 24 (1H, m, H-3′), 4. 24 (1H, m, H-4′), 4. 04 (1H, m, H-2′), 3. 88 (1H, m, H-5′), 3. 48 (1H, d, *J*=11. 5 Hz, H-24), 3. 05 (1H, m, H-5), 2. 64 (1H, m, H-8), 2. 55 (1H, m, H-22b), 2. 44 (1H, m, H-2b), 2. 25 (2H, m, H-7), 2. 25 (1H, m, H-17), 2. 13 (1H, m, H-11b), 2. 04 (2H, m, H-23), 1. 96 (1H, m, H-2a), 1. 90 (1H, m, H-15b), 1. 86 (1H, m, H-11a), 1. 85 (1H, m, H-15a), 1. 84 (1H, m, H-22a), 1. 81 (3H, s, H-29), 1. 65 (1H, m, H-1b), 1. 65 (1H, m, H-12b), 1. 55 (3H, s, H-21), 1. 55 (3H, s, H-28), 1. 45 (1H, m, H-12a), 1. 33 (3H, s, H-18), 1. 31 (3H, s, H-27), 1. 29 (3H, s, H-26), 1. 21 (1H, m, H-1a), 0. 97 (3H, s, H-30), 0. 65 (1H, d, *J*=5. 1 Hz, H-19b), 0. 08 (1H, d, *J*=5. 1 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 29. 4 (C-1), 30. 5 (C-2), 88. 1 (C-3), 41. 5 (C-4), 58. 1 (C-5), 211. 6 (C-6), 41. 8 (C-7), 43. 0 (C-8), 21. 9 (C-9), 30. 6 (C-10), 26. 8 (C-11), 33. 6 (C-12), 45. 6 (C-13), 47. 5 (C-14), 44. 6 (C-15), 73. 3 (C-16), 58. 0 (C-17), 18. 8 (C-18), 22. 3 (C-19), 87. 5 (C-20), 28. 9 (C-21), 35. 3 (C-22), 27. 2 (C-23), 82. 0 (C-24), 71. 7 (C-25), 27. 4 (C-26), 28. 5 (C-27), 19. 5 (C-28), 26. 9 (C-29), 15. 6 (C-30), 107. 3 (C-1′), 76. 2 (C-2′), 79. 1 (C-3′), 72. 2 (C-4′), 78. 7 (C-5′), 63. 5 (C-6′)。该化合物数据与文献[8]报道的数据基本一致，故鉴定化合物**6**为黄芪叶苷A。

化合物**7**：白色无定形粉末；ESI-MS *m/z* 653 $[M+H]^+$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 00 (1H, m, H-16), 5. 00 (1H, d, *J*=7. 5 Hz, H-1′), 4. 57 (2H, m, H-6′), 4. 41 (1H, dd, *J*=11. 7, 5. 1 Hz, H-4′), 4. 25 (1H, d, *J*=8. 2 Hz, H-3′), 4. 08 (1H, d, *J*=7. 7 Hz, H-2′), 3. 96 (1H, m, H-5′), 3. 87 (1H, dd, *J*=8. 5, 5. 6 Hz, H-24), 3. 64 (1H, dd, *J*=15. 8, 4. 1 Hz, H-3), 3. 09 (1H, m, H-6), 2. 52 (1H, d, *J*=7. 7 Hz, H-5), 2. 52 (1H, d, *J*=7. 6 Hz, H-17), 2. 30 (1H, m, H-12b), 2. 10 (1H, m, H-12a), 2. 10 (1H, m, H-15b), 2. 05 (2H, m, H-23), 2. 01 (3H, s, H-28), 1. 81 (2H, m, H-11), 1. 75 (1H, m, H-1b), 1. 75 (1H, m, H-8), 1. 75 (1H, m, H-15a), 1. 65 (1H, m, H-2b), 1. 65 (2H, m, H-22), 1. 60 (2H, m, H-7), 1. 57 (3H, s, H-26), 1. 40 (3H, s, H-18), 1. 33 (3H, s, H-29), 1. 30 (3H, s, H-27), 1. 28 (3H, s, H-21), 1. 15 (1H, m, H-1a), 1. 10 (1H, m, H-2a), 0. 99 (3H, s, H-30), 0. 54 (1H, d, *J*=3. 5 Hz, H-19b), 0. 21 (1H, d, *J*=3. 5 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 32. 3 (C-1), 30. 1 (C-2), 88. 9 (C-3), 42. 5 (C-4), 53. 9 (C-5), 67. 9 (C-6), 38. 5 (C-7), 46. 9 (C-8), 20. 8 (C-9), 29. 4 (C-11), 33. 3 (C-12), 44. 9 (C-13), 46. 0 (C-14), 46. 5 (C-15), 73. 3 (C-16), 58. 2 (C-17), 21. 4 (C-18), 30. 4 (C-19), 87. 1 (C-20), 27. 0 (C-21), 34. 8 (C-22), 26. 3 (C-23), 81. 6 (C-24), 71. 2 (C-25), 28. 1 (C-26), 28. 5 (C-27), 28. 9 (C-28), 16. 6 (C-29), 20. 1 (C-30), 106. 9 (C-1′), 75. 8 (C-2′), 78. 6 (C-3′), 71. 7 (C-4′), 78. 1 (C-5′), 62. 94 (C-6′)。该化合物数据与文献[12]报道的数据基本一致，故鉴定化合物**7**为astraverrucin Ⅰ。

化合物**8**：白色无定形粉末；ESI-MS *m/z* 651 $[M-H]^-$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 5. 01 (1H, m, H-16), 5. 01 (1H, d, *J*=7. 5 Hz, H-1′), 4. 57 (1H, m, H-6′b), 4. 42 (1H, m, H-6′a), 4. 24(1H, m, H-3′), 4. 08 (1H, m, H-2′), 3. 97 (1H, m, H-5′), 3. 87 (1H, d, *J*=5. 9 Hz, H-24), 3. 74 (1H, m, H-6), 3. 65 (1H, m, H-3), 3. 59 (1H, m, H-8), 3. 10 (2H, m, H-22), 2. 53 (1H, d, *J*=7. 4 Hz, H-17), 2. 47 (2H, m, H-23), 2. 30 (1H, m, H-2b), 2. 24 (1H, m, H-4′), 2. 10 (1H, m, H-15b), 2. 01 (3H, s, H-28), 1. 81 (2H, m, H-11), 1. 74 (1H, m, H-5), 1. 70 (1H, m, H-2a), 1. 65 (1H, m, H-12b), 1. 64 (1H, m, H-7b), 1. 60 (1H, m, H-1b), 1. 57 (3H, s, H-26), 1. 41 (3H, s, H-18), 1. 39 (1H, m, H-12a), 1. 33 (3H, s, H-29), 1. 31 (1H, m, H-15a), 1. 30 (3H, s, H-27), 1. 28 (3H, s, H-21), 1. 20 (1H, m, H-7a), 1. 15 (1H, m, H-1a), 0. 99 (3H, s, H-30), 0. 55 (1H, d, *J*=3. 9 Hz, H-19b), 0. 22 (1H, d, *J*=3. 9 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 32. 4 (C-1), 30. 1 (C-2), 87. 6 (C-3), 42. 5 (C-4), 53. 9 (C-5), 67. 9 (C-6), 38. 5 (C-7), 46. 9 (C-8), 20. 9 (C-9), 29. 4 (C-10), 26. 3 (C-11), 33. 3 (C-12), 44. 9 (C-13), 45. 9 (C-14), 46. 0 (C-15), 73. 4 (C-16),

58. 3 (C-17), 21. 4 (C-18), 30. 4 (C-19), 87. 1 (C-20), 27. 0 (C-21), 34. 8 (C-22), 26. 3 (C-23), 81. 6 (C-24), 71. 2 (C-25), 28. 1 (C-26), 28. 5 (C-27), 28. 9 (C-28), 16. 6 (C-29), 20. 1 (C-30), 106. 9 (C-1′), 75. 9 (C-2′), 78. 7 (C-3′), 71. 7 (C-4′), 78. 1 (C-5′), 62. 9 (C-6′)。该化合物数据与文献[13-14]数据基本一致，故鉴定化合物**8**为 cycloaraloside A。

化合物**9**：白色无定形粉末；ESI-MS *m/z* 693 $[M-H]^-$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 4. 99 (1H, m, H-16), 4. 97 (1H, d, *J*=7. 5 Hz, H-1′), 4. 60 (1H, m, H-6′b), 4. 59 (1H, m, H-6), 4. 42 (1H, m, H-6′a), 4. 24 (1H, m, H-3′), 4. 24 (1H, m, H-4′), 4. 05 (1H, m, H-2′), 3. 87 (1H, d, *J*=9. 1, 5. 4 Hz, H-24), 3. 87 (1H, m, H-5′), 3. 58 (1H, m, H-3), 3. 08 (1H, m, H-22b), 2. 51 (1H, m, H-17), 2. 43 (2H, m, H-2), 2. 29 (1H, m, H-8), 2. 29 (1H, m, H-23b), 2. 10 (1H, m, H-11b), 2. 03 (3H, s, 6-CH_3CO), 2. 00 (1H, m, H-23a), 1. 94 (1H, m, H-15b), 1. 80 (1H, m, H-11a), 1. 79 (1H, m, H-5), 1. 75 (1H, m, H-7b), 1. 75 (1H, m, H-15a), 1. 70 (1H, m, H-12b), 1. 65 (1H, m, H-1b), 1. 60 (1H, m, H-22a), 1. 56 (3H, s, H-29), 1. 45 (1H, m, H-7a), 1. 45 (1H, m, H-12a), 1. 41 (3H, s, H-21), 1. 34 (3H, s, H-28), 1. 32 (3H, s, H-27), 1. 30 (3H, s, H-26), 1. 21 (1H, m, H-1a), 1. 17 (3H, s, H-18), 0. 97 (3H, s, H-30), 0. 48 (1H, d, *J*= 4. 4 Hz, H-19b), 0. 17 (1H, d, *J*=4. 4 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 28. 8 (C-1), 29. 7 (C-2), 87. 7 (C-3), 42. 0 (C-4), 49. 9 (C-5), 70. 6 (C-6), 33. 1 (C-7), 45. 2 (C-8), 20. 6 (C-9), 29. 7 (C-10), 25. 8 (C-11), 33. 3 (C-12), 44. 9 (C-13), 45. 9 (C-14), 46. 2 (C-15), 73. 2 (C-16), 58. 1 (C-17), 21. 7 (C-18), 31. 8 (C-19), 87. 1 (C-20), 28. 5 (C-21), 34. 8 (C-22), 26. 4 (C-23), 81. 6 (C-24), 71. 2 (C-25), 27. 0 (C-26), 28. 1 (C-27), 19. 8 (C-28), 26. 9 (C-29), 16. 5 (C-30), 106. 9 (C-1′), 75. 7 (C-2′), 78. 7 (C-3′), 71. 7 (C-4′), 78. 3 (C-5′), 62. 9 (C-6′), 170. 2 (CH_3CO), 21. 0 (CH_3CO)。该化合物数据与文献[15]报道的数据基本一致，故鉴定化合物**9**为黄芪叶苷 D。

化合物**10**：白色无定形粉末；ESI-MS *m/z* 697 $[M+HCOO]^-$；^{1}H-NMR (600 MHz, C_5D_5N) *δ*: 4. 89 (1H, d, *J*=8. 0 Hz, H-1′), 4. 69 (1H, dd, *J*=13. 1, 7. 7 Hz, H-16), 4. 48 (2H, m, H-6′), 4. 46 (1H, m, H-5′), 4. 29 (1H, m, H-3′), 4. 19 (1H, m, H-4′), 4. 12 (1H, dd, *J*= 10. 5, 6. 0 Hz, H-24), 4. 01 (1H, d, *J*=9. 0, 8. 0 Hz, H-2′), 3. 67 (1H, ddd, *J*=11. 5, 9. 0, 3. 0 Hz, H-6), 3. 58 (1H, dd, *J*=11. 0, 4. 5 Hz, H-3), 2. 53 (1H, m, H-22b), 2. 41 (2H, m, H-2), 2. 20 (1H, d, *J*=7. 5 Hz, H-17), 2. 18 (1H, m, H-15b), 2. 07 (1H, m, H-23b), 2. 02 (3H, s, H-28), 1. 98 (1H, dd, *J*=11. 0, 4. 5 Hz, H-8), 1. 96 (1H, m, H-11b), 1. 93 (3H, s, H-18), 1. 86 (1H, m, H-23a), 1. 85 (1H, m, H-7b), 1. 84 (1H, m, H-22a), 1. 82 (1H, m, H-15a), 1. 77 (1H, m, H-5), 1. 77 (1H, m, H-12b), 1. 72 (1H, m, H-12a), 1. 59 (1H, m, H-7a), 1. 50 (1H, m, H-1b), 1. 48 (3H, s, H-21), 1. 37 (3H, s, H-27), 1. 35 (3H, s, H-29), 1. 27 (3H, s, H-26), 1. 21 (1H, m, H-11a), 1. 14 (1H, m, H-1a), 0. 88 (3H, s, H-30), 0. 42 (1H, d, *J*=4. 0 Hz, H-19b), 0. 14 (1H, d, *J*=4. 0 Hz, H-19a)；^{13}C-NMR (150 MHz, C_5D_5N) *δ*: 32. 4 (C-1), 30. 1 (C-2), 89. 1 (C-3), 42. 6 (C-4), 53. 9 (C-5), 68. 3 (C-6), 38. 4 (C-7), 47. 2 (C-8), 21. 1 (C-9), 29. 5 (C-10), 26. 4 (C-11), 33. 4 (C-12), 46. 5 (C-13), 46. 7 (C-14), 49. 6 (C-15), 73. 3 (C-16), 56. 6 (C-17), 21. 3 (C-18), 30. 8 (C-19), 87. 7 (C-20), 29. 1 (C-21), 38. 4 (C-22), 25. 7 (C-23), 87. 8 (C-24), 70. 7 (C-25), 26. 2 (C-26), 26. 8 (C-27), 28. 9 (C-28), 16. 7 (C-29), 20. 4 (C-30), 106. 7 (C-1′), 75. 8 (C-2′), 78. 5 (C-3′), 71. 7 (C-4′), 77. 9 (C-5′), 62. 8 (C-6′)。该化合物数据与文献[16-19]报道的数据基本一致，故鉴定化合物**10**为 astralanosaponin D。

化合物**11**：白色无定形粉末；ESI-MS *m/z* 457 $[M+H]^+$；^{1}H-NMR (400 MHz, CD_3OD) *δ*: 5. 32 (1H, dd, *J*=7. 0, 4. 0 Hz, H-12), 4. 10 (1H, d, *J*=11. 0 Hz, H-24b), 3. 40 (1H, d, *J*=11. 0 Hz, H-24a), 3. 30 (1H, dd, *J*=7. 0, 4. 0 Hz, H-3), 2. 00 (1H, d, *J*=3. 0 Hz, H-5), 1. 26 (3H, s, H-27), 1. 20 (3H, s, H-23), 1. 00 (3H, s, H-29), 0. 98 (3H, s, H-26), 0. 97 (3H, s, H-30), 0. 96 (3H, s, H-25), 0. 87 (3H, s, H-28)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 39. 6 (C-1), 28. 4 (C-2), 81. 2 (C-3), 43. 6 (C-4), 57. 2 (C-5), 19. 8 (C-6), 34. 2 (C-7), 40. 9 (C-8), 48. 8 (C-9), 37. 9 (C-10), 24. 8 (C-11), 125. 1 (C-12), 142. 8 (C-13), 43. 0 (C-14), 26. 2 (C-15), 28. 3 (C-16), 48. 4 (C-17), 48. 6 (C-18), 47. 6 (C-19), 35. 1 (C-20), 51. 7 (C-21), 219. 7 (C-22), 23. 2 (C-23), 65. 3 (C-24), 16. 5 (C-25), 17. 3 (C-26), 25. 8 (C-27), 25. 6 (C-28), 32. 2 (C-29), 21. 1 (C-30)。该化合物数据与文献[19]

数据基本一致，故鉴定化合物**11**为大豆皂醇E。

化合物**12**：无色针状结晶（$CHCl_3$）；ESI-MS *m/z* 459 $[M+H]^+$；^{1}H-NMR (400 MHz, DMSO-d_6) δ: 5. 17 (1H, m, H-12), 5. 00 (1H, m, H-3), 3. 80 (1H, dd, *J*=11. 0, 2. 8 Hz, H-24b), 3. 28 (1H, dd, *J*=11. 0, 2. 8 Hz, H-24a), 3. 25 (1H, m, H-21), 1. 07 (3H, s, H-23), 1. 06 (3H, s, H-30), 0. 98 (3H, s, H-29), 0. 89 (3H, s, H-26), 0. 88 (3H, s, H-25), 0. 85 (3H, s, H-28), 0. 76 (3H, s, H-27)；^{13}C-NMR (100 MHz, DMSO-d_6) δ: 38. 0 (C-1), 27. 1 (C-2), 78. 5 (C-3), 41. 5 (C-4), 55. 2 (C-5), 18. 5 (C-6), 32. 7 (C-7), 38. 7 (C-8), 47. 0 (C-9), 36. 2 (C-10), 23. 1 (C-11), 121. 4 (C-12), 144. 0 (C-13), 42. 0 (C-14), 25. 4 (C-15), 30. 1 (C-16), 32. 5 (C-17), 45. 9 (C-18), 44. 4 (C-19), 36. 8 (C-20), 73. 9 (C-21), 41. 1 (C-22), 22. 7 (C-23), 62. 9 (C-24), 15. 5 (C-25), 16. 4 (C-26), 20. 2 (C-27), 27. 7 (C-28), 28. 2 (C-29), 24. 9 (C-30)。该化合物数据与文献[20]报道的数据基本一致，故鉴定化合物**12**为3*β*,21*α*,24-三羟基-齐墩果-12-烯。

化合物**13**：白色不定形粉末；ESI-MS *m/z* 475 $[M+H]^+$；^{1}H-NMR (400 MHz, C_5D_5N) δ: 5. 17 (1H, dd, *J*=7. 0, 3. 0 Hz, H-12), 4. 50 (1H, d, *J*=11. 0 Hz, H-24b), 3. 70 (1H, d, *J*=11. 0 Hz, H-24a), 3. 60 (1H, m, H-22), 1. 55 (3H, s, H-23), 1. 47 (3H, s, H-29), 1. 27 (3H, s, H-28), 1. 25 (3H, s, H-27), 1. 02 (3H, s, H-26), 0. 94 (3H, s, H-25)；^{13}C-NMR (100 MHz, C_5D_5N) δ: 39. 0 (C-1), 28. 5 (C-2), 80. 1 (C-3), 43. 2 (C-4), 56. 4 (C-5), 19. 2 (C-6), 33. 6 (C-7), 40. 0 (C-8), 48. 2 (C-9), 37. 1 (C-10), 24. 1 (C-11), 122. 5 (C-12), 145. 0 (C-13), 42. 4 (C-14), 26. 5 (C-15), 29. 0 (C-16), 38. 3 (C-17), 44. 9 (C-18), 41. 6 (C-19), 36. 6 (C-20), 37. 4 (C-21), 75. 7 (C-22), 23. 6 (C-23), 64. 6 (C-24), 16. 3 (C-25), 17. 1 (C-26), 25. 6 (C-27), 21. 2 (C-28), 73. 1 (C-29), 24. 5 (C-30)。该化合物数据与文献[21]报道的数据基本一致，故鉴定化合物**13**为3*β*,22*β*,24,29-四羟基齐墩果-12-烯。

化合物**14**：白色粉末；ESI-MS *m/z* 1029 $[M+H]^+$；^{1}H-NMR (400 MHz, C_5D_5N) δ: 6. 43 (1H, br s, H-1‴), 5. 90 (1H, d, *J*=7. 8 Hz, H-1″), 5. 16 (1H, d, *J*=3. 0 Hz, H-12), 5. 00 (1H, d, *J*=7. 7 Hz, H-1′), 4. 25 (1H, d, *J*=11. 0 Hz, H-24b), 3. 80 (2H, br s, H-2⁗), 3. 35 (1H, m, H-3), 3. 30 (1H, d, *J*=11. 0 Hz, H-24a), 1. 85 (3H, m, H-6‴), 1. 45 (3H, s, H-23), 1. 22 (3H, s, H-27), 1. 12 (3H, s, H-30), 1. 02 (3H, s, H-28), 0. 88 (3H, s, H-29), 0. 82 (3H, s, H-26), 0. 62 (3H, s, H-25)；^{13}C-NMR (100 MHz, C_5D_5N) δ: 38. 5 (C-1), 26. 6 (C-2), 91. 6 (C-3), 43. 7 (C-4), 56. 1 (C-5), 18. 5 (C-6), 32. 9 (C-7), 40. 0 (C-8), 47. 6 (C-9), 36. 3 (C-10), 24. 0 (C-11), 123. 0 (C-12), 144. 0 (C-13), 41. 9 (C-14), 26. 6 (C-15), 27. 2 (C-16), 36. 8 (C-17), 44. 7 (C-18), 46. 2 (C-19), 30. 6 (C-20), 38. 5 (C-21), 79. 5 (C-22), 22. 8 (C-23), 63. 4 (C-24), 15. 6 (C-25), 17. 0 (C-26), 26. 2 (C-27), 21. 0 (C-28), 33. 6 (C-29), 27. 2 (C-30), 105. 3 (C-1′), 79. 2 (C-2′), 78. 1 (C-3′), 73. 8 (C-4′), 78. 4 (C-5′), 172. 4 (C-6′), 102. 0 (C-1″), 78. 7 (C-2″), 77. 8 (C-3″), 72. 4 (C-4″), 77. 5 (C-5″), 61. 4 (C-6″), 102. 1 (C-1‴), 72. 8 (C-2‴), 72. 9 (C-3‴), 74. 4 (C-4‴), 69. 5 (C-5‴), 19. 0 (C-6‴)。该化合物数据与文献[22]数据基本一致，故鉴定化合物**14**为豌豆皂苷Ⅰ。

化合物**15**：白色粉末；ESI-MS *m/z* 943 $[M+H]^+$；^{1}H-NMR (400 MHz, C_5D_5N) δ: 6. 42 (1H, br s, H-1‴), 5. 89 (1H, d, *J*=7. 7 Hz, H-1″), 5. 27 (1H, br s, H-12), 5. 00 (1H, d, *J*=7. 9 Hz, H-1′), 4. 25 (1H, d, *J*=11. 0 Hz, H-24b), 3. 70 (1H, m, H-22), 3. 38 (1H, d, *J*=11. 0 Hz, H-24a), 3. 37 (1H, dd, *J*=12. 5, 8. 0 Hz, H-3), 1. 78 (3H, s, H-6‴), 1. 46 (3H, s, H-23), 1. 27 (3H, s, H-30), 1. 26 (3H, s, H-27), 1. 20 (3H, s, H-28), 0. 97 (3H, s, H-29), 0. 92 (3H, s, H-26), 0. 66 (3H, s, H-25)；^{13}C-NMR (100 MHz, C_5D_5N) δ: 38. 6 (C-1), 26. 5 (C-2), 91. 6 (C-3), 44. 4 (C-4), 56. 3 (C-5), 18. 6 (C-6), 33. 4 (C-7), 40. 0 (C-8), 47. 8 (C-9), 36. 5 (C-10), 24. 1 (C-11), 122. 4 (C-12), 144. 9 (C-13), 43. 7 (C-14), 26. 7 (C-15), 33. 3 (C-16), 38. 0 (C-17), 45. 3 (C-18), 46. 8 (C-19), 30. 9 (C-20), 42. 4 (C-21), 75. 6 (C-22), 22. 9 (C-23), 63. 5 (C-24), 15. 7 (C-25), 17. 0 (C-26), 25. 7 (C-27), 21. 2 (C-28), 33. 3 (C-29), 28. 7 (C-30)；105. 3 (C-1′), 74. 4 (C-2′), 77. 5 (C-3′), 79. 2 (C-4′), 77. 9 (C-5′), 172. 6 (C-6′), 102. 0 (C-1″), 78. 5 (C-2″), 78. 1 (C-3″), 69. 8 (C-4″), 78. 7 (C-5″), 61. 4 (C-6″), 102. 1 (C-1‴), 72. 4 (C-2‴), 72. 8 (C-3‴), 73. 8 (C-4‴), 69. 5 (C-5‴), 19. 0 (C-6‴)。该化合物数据与文献[23]报道的数据基本一致，故鉴定该化合物为大豆皂醇B-3-*O*-*β*-*D*-葡萄糖醛酸基-(1→2)-*β*-*D*-葡萄糖基-(1→4)-*α*-*L*-鼠李糖苷。

4　讨论

国内外学者对膜荚黄芪叶的化学成分和药理作用进行了大量的研究，发现膜荚黄芪叶中含有三萜皂苷[24]、黄酮[25]和多糖[26]等多种活性成分。其中，膜荚黄芪叶中三萜皂苷类化合物具有抗病毒、降血压和调节免疫力等药理活性[27]，并且具有改善肾小管损伤、抑制核转录因子-κB（NF-κB）p65 表达[28]、保护胰腺[29]、抗炎[30]、抗衰老[27]及保护肝脏[31]的作用。本研究对膜荚黄芪叶的化学成分进行分离和鉴定，共分离得到 15 个化合物，其中 5 个化合物为首次从该属中分离得到，均为齐墩果烷型三萜皂苷。有学者对齐墩果烷型三萜皂苷进行研究，发现齐墩果烷型三萜皂苷具有较好的抗肝损伤活性[32]，该类化合物的代表齐墩果酸具有抗炎作用[33]，并已经作为保肝药物应用于临床[34]。此外，张宇等[35]对膜荚黄芪叶的药理作用进行了研究，实验结果表明膜荚黄芪叶对二甲苯引起的小鼠耳肿胀具有抑制作用，同时对 CCl_4 引起的急性肝损伤有保护作用。Su 等[36]发现黄芪甲苷能降低肝癌细胞抗凋亡蛋白的表达水平，抑制肝癌细胞侵袭能力。对膜荚黄芪叶化学成分的研究能够为其药理作用、临床应用研究及资源利用提供参考。

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