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论 著

# 膜荚黄芪中黄酮类化学成分研究

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**摘要** **目的**:研究膜荚黄芪中黄酮类化学成分。**方法**:采用硅胶柱色谱和HPLC制备色谱方法分离纯化得到单体化合物,采用有机波谱方法鉴定化合物结构。**结果**:从膜荚黄芪乙醇提取物中分离得到8个黄酮类化合物,分别为2′,7-二羟基-3′,4′-二甲氧基异黄烷-2′-O-β-D-吡喃葡萄糖苷(1),3′,4′-二甲基异黄烷(2),芒柄花素(3),芒柄花素-7-O-β-D-葡萄糖苷(4),毛蕊异黄酮(5),(6aR,11aR)3-羟基-9,10-二甲氧基紫檀烷(6),(6aR,11aR)9,10-二甲氧基紫檀烷-3-O-β-D-葡萄糖苷(7),7,2′-二羟基-3′,4′-二甲氧基异黄烷-7-O-β-D-葡萄糖苷(8)。**结论**:化合物1为首次从该属植物中分离得到。

**关键词** 膜荚黄芪;化学成分;色谱分离;黄酮类;2′,7-二羟基-3′,4′-二甲氧基异黄烷-2′-O-β-D-吡喃葡萄糖苷
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## Studies on flavonoids and related constituents from *Astragalus membranceus*(Fisch) Bge

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**Abstract** **Objective:** To study flavonoids and related constituents from *Astragalus membranceus* (Fisch) Bge. **Methods:** Chemical constituents were isolated and purified by repeated column chromatography (silica geland preparative HPLC). Their structures were elucidated by spectral data analysis. **Results:** Eight compounds (1-8) were isolated and their structures were identified by comparing their spectral data with literature values as follows: sphaerophyside SB (1), isomucronulatol (2), formononetin (3), formononetin-7-O-β-D-glycoside(4), calycosin(5), methylnissolin(6), (6aR,11aR) 9,10-dimethoxypterocarpan-3-O-β-D- glycoside(7), 7,2′-dihydroxy-3′,4′-dimethoxy-isoflavane-7-O-β-D-glycoside(8). **Conclusion:** Compounds 1 could be isolated from this plant for the first time.

**Key words** *Astragalus membranceus*(Fisch) Bge; chemical constituents; chromatographic separation; flavonoids; sphaerophyside SB

膜荚黄芪(*Astragalus membranceus*(Fisch)Bge)是豆科黄芪属植物,是黄芪的正品之一,为常用中药[1],具有补气固表,利尿脱毒,益气补中之功效[2]。用于久泻脱肛,久溃不敛,内热消渴,慢性肾炎蛋白尿糖尿病等[3]。黄芪的化学成分主要为三萜皂苷类、黄酮类和多糖类[4],本文主要对膜荚黄芪中黄酮类成分进行了研究。

## 1 材料与方法

1.1 仪器、试剂及材料 核磁共振仪:Bruker AV 400 instrument (TMS内标);液质联用色谱仪:Alliance 2695, Quattro Micro TM ESI (Waters);半制备高效液相色谱仪:日本分光公司(JASCO),PU-2089(泵),RI-2031和UV-2075(检测器);制备HPLC色谱柱:YMC-Pack SIL SL12S05-2510WT(10 mm × 250 mm);氘代试剂(ALDRICH公司);柱色谱和薄层色谱用硅胶均系青岛海洋化工厂生产,所用试剂均系分析纯。

膜荚黄芪于2010年购买于陕西,由天津医科大学药学院唐生安副教授鉴定,标本(D20100415)存放于天津医科大学药学院。

1.2 提取分离 将黄芪清膏600 g,加入95%乙醇(1 000 mL)浸泡3次,合并浸泡液,减压浓缩浸泡液的总提取物143 g。将总提物混悬于水(2 000 mL)中,用乙酸乙酯(2 000 mL)萃取3次,合并萃取液,浓缩干燥称重,得乙醇萃取物8 g(0101)。

0101经HW-40柱分离,以二氯甲烷-甲醇(1:1)为流动相洗脱,得到6个组分(0401-0406);0404经HPLC纯化,以甲醇-水(8:2)为流动相,得到化合物3(14.1 mg);0403经HPLC纯化,以甲醇-水(8:2)为流动相,得到10个组分(0501-0510)。0503经GPC纯化,以甲醇为流动相,得到12个组分(1101-1112),其中1101为化合物4(38.9 mg),1109经HPLC纯化,以甲醇-水(7:3)为流动相,得到化合物7(17.4 mg);0504经GPC纯化,以甲醇为流动相,得到化合物5(34.2 mg);0505经GPC纯化,以甲醇为流动相,得到11个组分(1501-1511),1508经制备薄

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层色谱分离，以二氯甲醇-甲醇(95:5)为展开剂，得到化合物2（9.5 mg）、化合物6（2.5 mg）；0405经GPC纯化，以甲醇为流动相，得到化合物1(2.0 mg)；0406经GPC纯化，以甲醇为流动相，得到化合物8(5.1 mg)。

## 2 结果

从膜荚黄芪中分离得到8个化合物。

2.1 化合物1 2′,7-二羟基-3′,4′-二甲氧基异黄烷-2′-O-β-D-吡喃葡萄糖苷，白色粉末。ESI-MS*m/z*481 $[M+H]^+$(分子式 $C_{23}H_{28}O_{11}$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:2.64 (1H, dd, *J* = 16.0Hz,3.5 Hz, H-4), 2.79 (1H, dd, *J* = 16.0Hz,3.5 Hz, H-4), 3.58 (1H, m, H-3), 3.72 (3H, s, 3′-$OCH_3$), 3.75 (3H, s, 4′-$OCH_3$), 3.78 (1H, t, *J* = 10.0Hz, H-2), 4.27 (1H, br.d, *J* = 10.0Hz, H-2), 4.87 (1H, d, *J* = 6.7Hz, H-1″), 6.18 (1H, br.d, H-8), 6.28 (1H, d, *J* = 8.1Hz, H-6), 6.80 (1H, d, *J* = 8.7Hz, H-5′), 6.85 (1H, d, *J* = 8.3Hz, H-5), 6.90 (1H, d, *J* = 8.7Hz, H-6′); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 69.6 (C-2), 30.3 (C-3), 30.8 (C-4), 130.0 (C-5), 107.8 (C-6), 156.4 (C-7), 102.6 (C-8), 154.7 (C-9), 112.9(C-10), 128.7 (C-1′), 147.6 (C-2′), 141.2 (C-3′), 152.1 (C-4′), 108.6 (C-5′), 121.6 (C-6′), 103.4 (C-1″), 73.9 (C-2″), 77.4 (C-3″), 70.2 (C-4″), 76.4 (C-5″), 61.3 (C-6″), 60.5 (3′-$OCH_3$), 55.8 (4′-$OCH_3$)。

2.2 化合物2 3′,4′-二甲基异黄烷，白色粉末。ESI-MS*m/z*319 $[M+H]^+$(分子式 $C_{17}H_{18}O_6$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:2.74 (1H, dd, *J* = 15.4Hz,4.6 Hz, H-4), 2.85 (1H, m, H-4), 3.32 (1H, m, H-3), 3.67 (3H, s, H-3′-$OCH_3$), 3.75 (3H, s, 4′-$OCH_3$), 3.92 (1H, t, *J* = 10.0Hz, H-2), 4.16 (1H, br.d, *J* = 10.3Hz, H-2), 6.18 (1H, d, *J* = 2.1Hz, H-8), 6.29 (1H, d, *J* = 2.2Hz, H-5), 6.46 (1H, d, *J* = 2.3Hz, H-6), 6.78 (1H, d, J = 8.6Hz, H-5′), 6.86 (1H, d, *J* = 8.2Hz, H-6′), 8.90 (1H, s, 2′-OH), 9.12 (1H, s, 7-OH); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 69.1 (C-2), 31.4 (C-3), 29.7 (C-4), 130.0 (C-5), 108.0 (C-6), 156.4 (C-7), 102.5 (C-8), 154.5 (C-9), 112.4(C-10), 121.0 (C-1′), 148.1 (C-2′), 136.1 (C-3′), 151.6 (C-4′), 103.1 (C-5′), 121.4 (C-6′), 60.2 (3′-$OCH_3$), 55.6 (4′-$OCH_3$)。

2.3 化合物3 芒柄花素，白色针晶。ESI-MS*m/z*269 $[M+H]^+$(分子式 $C_{16}H_{12}O_4$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:3.78 (3H, s, -$OCH_3$), 6.87 (1H, s, H-8), 6.94 (1H, dd, *J* = 6.9Hz,1.9 Hz, H-6), 6.99 (2H, d, *J* = 8.6Hz, H-3′,5′), 7.51 (2H, d, *J* = 8.6Hz, H-2′,6′), 7.98 (1H, d, *J* = 8.8Hz, H-5), 8.34 (1H, s, H-2), 10.82 (1H, s, 7-OH); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 153.1 (C-2), 124.2 (C-3), 174.6 (C-4), 127.3 (C-5), 115.2 (C-6), 162.6 (C-7), 102.1 (C-8), 157.4 (C-9), 116.6(C-10), 123.1 (C-1′), 130.0 (C-2′), 113.6 (C-3′), 158.9 (C-4′), 113.6 (C-5′), 130.0 (C-6′), 55.1 (4′-$OCH_3$)。

2.4 化合物4 芒柄花素-7-O-β-D-葡萄糖苷，白色针晶。ESI-MS*m/z*431 $[M+H]^+$ (分子式 $C_{22}H_{22}O_9$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:3.79 (3H, s, -$OCH_3$), 5.10 (1H, d, *J* = 5.9Hz, H-1″), 7.00 (2H, d, *J* = 8.3Hz, H-3′,5′), 7.15 (1H, d, *J* = 8.9Hz, H-6), 7.25 (1H, m, H-8), 7.54 (2H, d, *J* = 8.2Hz, H-2′,6′), 8.06 (1H, d, *J* = 8.8Hz, H-5), 8.44 (1H, s,H-2); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 154.1 (C-2), 123.8 (C-3), 175.1 (C-4), 127.4 (C-5), 116.1 (C-6), 161.9 (C-7), 103.9 (C-8), 157.5 (C-9), 118.9(C-10), 124.5 (C-1′), 130.0 (C-2′), 114.1 (C-3′), 159.5 (C-4′), 114.1 (C-5′), 130.0 (C-6′), 100.5 (C-1″), 73.6 (C-2″), 77.0 (C-3″), 69.6 (C-4″), 77.2 (C-5″), 61.1 (C-6″), 55.6 (4′-$OCH_3$)。

2.5 化合物5 毛蕊异黄酮，白色针晶。ESI-MS*m/z*285 $[M+H]^+$ (分子式 $C_{16}H_{12}O_5$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:3.80 (3H, s, -$OCH_3$),6.87 (1H, br.s, H-6), 6.93 (1H, br.s, H-6), 6.95 (2H, br.s, H-5′,6′), 7.06 (1H, br.s,H-2′), 7.97 (1H, d, *J* = 8.8Hz, H-5), 8.29 (1H, s, H-2); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 153.0 (C-2), 123.3 (C-3), 174.5 (C-4), 127.3 (C-5), 115.1 (C-6), 162.5 (C-7), 102.1 (C-8), 157.3 (C-9), 116.6 (C-10), 124.7 (C-1′), 116.4 (C-2′), 146.0 (C-3′), 147.5 (C-4′), 111.9 (C-5′), 119.7 (C-6′), 55.6 (4′-$OCH_3$)。

2.6 化合物6 (6aR,11aR)3-羟基-9,10-二甲氧基紫檀烷，白色粉末。ESI-MS*m/z*301 $[M+H]^+$ (分子式 $C_{17}H_{16}O_5$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:3.61 (1H, d, *J* = 6.0Hz, H-6a), 3.70 (3H, s, 10-$OCH_3$), 3.73 (3H, s, 9-$OCH_3$), 4.23 (1H, dd, *J* = 10.0Hz,6.0 Hz, H-6), 5.56 (1H, d, *J* = 5.8Hz, H-11a), 6.25 (1H, br.d, H-4), 6.48 (1H, dd, *J* = 8.3Hz,2.0Hz, H-2), 6.52 (1H, d, *J* = 8.2Hz, H-8), 6.98 (1H, d, *J* = 8.1Hz, H-7), 7.30 (1H, d, *J* = 8.4Hz, H-1), 9.65 (1H, br.d, 3-OH); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 132.1 (C-1), 109.7 (C-2), 158.8 (C-3), 102.7 (C-4), 156.2 (C-4a), 65.6 (C-6), 39.2 (C-6a), 121.8 (C-6b), 118.7 (C-7), 104.9 (C-8), 152.7 (C-9), 133.3(C-10), 151.0 (C-11), 78.5 (C-11a), 111.0 (C-11b), 56.0 (9-$OCH_3$), 59.8 (10-$OCH_3$)。

2.7 化合物7 (6aR,11aR)9,10-二甲氧基紫檀烷-3-O-β-D-葡萄糖苷，白色针晶。ESI-MS*m/z*463 [M+

H]$^+$ (分子式 $C_{23}H_{26}O_{10}$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:3.71 (1H, m, H-6a), 3.73 (3H, s, 10-$OCH_3$), 3.79 (3H, s, 9-$OCH_3$), 4.28 (1H, d, $J$ = 7.1Hz, H-6), 4.85 (1H, d, $J$ = 7.4Hz, H-1′), 5.63 (1H, d, $J$ = 6.5Hz, H-11a), 6.53 (1H, m, H-8), 6.55 (1H, d, $J$ = 3.2Hz, H-4), 6.72 (1H, d, $J$ = 8.6Hz, H-2), 7.01 (1H, d, $J$ = 8.6Hz, H-7), 7.42 (1H, d, $J$ = 8.5Hz, H-1); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 132.0 (C-1), 110.4 (C-2), 158.5 (C-3), 103.9 (C-4), 156.1 (C-4a), 65.7 (C-6), 39.2 (C-6a), 121.5 (C-6b), 118.7 (C-7), 105.1 (C-8), 152.7 (C-9), 133.3(C-10), 151.0 (C-11), 78.2 (C-11a), 114.0 (C-11b), 100.2 (C-1′), 73.1 (C-2′), 76.5 (C-3′), 69.6 (C-4′), 77.0 (C-5′), 60.6 (C-6′), 59.8 (9-$OCH_3$), 56.0 (10-$OCH_3$)。

2.8 化合物 8 7,2′-二羟基-3′,4′-二甲氧基异黄烷-7-O-β-D-葡萄糖苷,白色粉末。ESI-MS$m/z$481 [M+H]$^+$(分子式 $C_{23}H_{28}O_{11}$)。$^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta_H$:2.81 (1H, dd, $J$ = 15.8Hz,4.7 Hz, H-4), 2.94 (1H, dd, $J$ = 15.9Hz,5.2 Hz, H-4), 3.19 (1H, t, $J$ = 5.5Hz, H-2"), 3.46 (1H, t, $J$ = 5.9Hz, H-3), 3.69 (3H, s, 3′-$OCH_3$), 3.75 (3H, s, 4′-$OCH_3$), 3.97 (1H, t, $J$ = 9.9Hz, H-2), 4.20 (1H, d, $J$ = 10.1Hz, H-2), 4.77 (1H, d, $J$ = 9.4Hz, H-1"), 5.25 (1H, d, $J$ = 4.6Hz, H-6), 6.47 (1H, br.s, H-5′), 6.54 (1H, d, $J$ = 8.2Hz, H-8), 6.79 (1H, d, $J$ = 8.6Hz, H-6′), 7.00 (1H, d, $J$ = 8.4Hz, H-5); $^{13}$C-NMR (DMSO-$d_6$, 100MHz)$\delta_C$: 69.7 (C-2), 31.8 (C-3), 29.5 (C-4), 130.5 (C-5), 109.3 (C-6), 157.2 (C-7), 104.4 (C-8), 154.9 (C-9), 116.2(C-10), 121.3 (C-1′), 148.6 (C-2′), 136.6 (C-3′), 152.1 (C-4′), 103.7 (C-5′), 121.9 (C-6′), 101.1 (C-1"), 73.7 (C-2"), 77.1 (C-3"), 70.2 (C-4"), 77.5 (C-5"), 61.2 (C-6"), 60.7 (3′-$OCH_3$), 56.1 (4′-$OCH_3$)。

## 3 讨论

本文对膜荚黄芪进行化学成分分离、纯化并得到单体化合物。通过核磁共振波谱、质谱等方法确定化合物的结构。结果表明,从膜荚黄芪分离得到8个化合物,$^1$H-NMR 和 $^{13}$C-NMR 数据与文献报道一致,依次鉴定为 2′,7-二羟基-3′,4′-二甲氧基异黄烷-2′-O-β-D-吡喃葡萄糖苷 (1)[5],3′,4′-二甲基异黄烷(2) [6],芒柄花素(3) [7],芒柄花素-7-O-β-D-葡萄糖苷(4) [8],毛蕊异黄酮(5) [9],(6aR,11aR)3-羟基-9,10-二甲氧基紫檀烷(6) [10],(6aR,11aR)9,10-二甲氧基紫檀烷-3-O-β-D-葡萄糖苷(7) [11],7,2′-二羟基-3′,4′-二甲氧基异黄烷-7-O-β-D-葡萄糖苷 (8) [12]。其中 1 为本属植物中首次分离得到,丰富了豆科黄芪属植物化学成分研究。黄酮类成分是黄芪中非常重要的药理活性成分,具有清除氧自由基、抑制脂质过氧化、维持血中 NO 浓度和保护缺血再灌注损伤等多种药理活性[13]。目前中药谱效关系研究中,以多成分协同作用为主,但各成分对药效的贡献程度不同。本文分离制备更多的单体化合物,进而对中药各单体化合物的药效关系进行研究,为进一步深入研究黄芪化学成分和药理作用提供理论基础。

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