文章编号:1001-6880(2014)Suppl-0022-03

猪殃殃中环烯醚萜苷和蒽醌苷类化学成分的研究

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摘　要:采用硅胶、反相硅胶和凝胶柱色谱进行分离、纯化,研究茜草科植物猪殃殃全草甲醇洗脱部位的化学成分。化合物经质谱和核磁等波谱分析方法确定结构得到 8 个化合物,分别为 6-*O*-乙酰鸡屎藤次苷(**1**),6α-羟基京尼平苷(**2**),京尼平苷酸(**3**),6β-羟基京尼平苷(**4**),交让木苷(**5**),6a-甲氧基京尼平苷酸(**6**),去乙酰基车叶草苷酸(**7**),光泽汀-3-*O*-葡萄糖苷(**8**)。化合物 **1**~**6** 为首次从拉拉藤中分离得到,其中化合物 **4**,**6** 是从该属中首次分到。

关键词:猪殃殃;环烯醚萜苷;6-*O*-乙酰鸡屎藤次苷;6β-羟基京尼平苷;交让木苷

中图分类号:R284.1　　**文献标识码**:A

Iridoid and Anthraquinone Glycosides in *Galium aparine* L.

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Abstract: To study the chemical constituents in methanol fraction of *Galium aparine* L., the 75% alcohol extract of *G. aparine* were subjected to silica gel, ODS and Sephadex LH-20 column chromatography. The isolates were identified with the physicochemical properties and spectra data. Eight compounds from *G. aparine*. were identified as 6-*O*-acetylscandoside(**1**), 6α-hydroxy geniposide(**2**), geniposidic acid(**3**), 6β-hydroxy geniposide(**4**), daphylloside(**5**), 6α-methoxy geniposidic acid(**6**), deacetylasperulosidic acid(**7**), lucidin-3-*O*-glucoside(**8**). Compounds **1-6** were isolated from *G. aparine* for the first time, and compounds **4** and **6** were firstly isolated from the genus *Galium*.

Key words: *Galium aparine*; iridoid glycoside; 6-*O*-acetylscandoside; 6β-hydroxy geniposide; daphylloside

猪殃殃,又名八仙草,拉拉藤,锯子草,小锯藤,小茜草,小飞扬藤,红丝线,血见愁,小舒筋,小血藤等,是茜草科拉拉藤属植物猪殃殃 *Galium aparine* L. 的全草,广泛分布于全国各地,为田间常见杂草。猪殃殃有清热解毒,利尿通淋,消肿止痛的功效,主治痈疽肿毒,乳腺炎,阑尾炎,水肿,感冒发热,痢疾,尿路感染,尿血,牙龈出血,刀伤出血[1]。拉拉藤属植物含有活性显著的环烯醚萜、蒽醌和黄酮类成分,前期的研究中发现猪殃殃含有蒽醌、酚酸、黄酮、三萜等成分[2],为进一步开发猪殃殃的药用价值,我们研究了该植物的化学成分,特别是甲醇洗脱部位的环烯醚萜苷等成分。从猪殃殃 75% 乙醇提取物的甲醇洗脱部位分离得到 8 个化合物,根据其理化性质和光谱数据分别鉴定为 6-*O*-乙酰鸡屎藤次苷(**1**),6α-羟基京尼平苷(**2**),京尼平苷酸(**3**),6β-羟基京尼平苷(**4**),交让木苷(**5**),6a-甲氧基京尼平苷酸(**6**),去乙酰基车叶草苷酸(**7**),光泽汀-3-*O*-葡萄糖苷(**8**)。化合物 **1**~**6** 为首次从拉拉藤中分离得到,其中化合物 **4**,**6** 是从该属中首次分到。

1　仪器与材料

Agilent MSD-Trap-XCT 质谱仪;Bruker 600 MHz AVIII 核磁共振仪(TMS 为内标);薄层色谱用硅胶和柱色谱硅胶均为烟台江友化工厂产品;ODS 为 Merck 公司产品;Sephadex LH-20 为 Pharmacia 公司产品;所用试剂均为分析纯。

猪殃殃药材于 2012 年 3 月采自上海川沙郊区,经鉴定为茜草科拉拉藤属植物猪殃殃 *Galium aparine* L. 的全草。

2　提取分离

猪殃殃药材 10 kg,用 75% 乙醇室温下浸泡 3 次,每次 48 h。浸提液减压浓缩得浸膏 1.0 kg,以甲醇溶解,拌 100~200 目硅胶(2 kg),减压蒸干后上硅胶柱色谱,依次用石油醚,二氯甲烷,醋酸乙酯及

收稿日期:2013-07-03　　接受日期:2014-02-25

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甲醇洗脱。甲醇洗脱流分(400 g)经硅胶柱色谱,用二氯甲烷:甲醇梯度洗脱(40∶1 ~20∶1 ~10∶1 ~2∶1 ~0∶1),TLC 检识,相同点合并,得到五个流分 Fr1-Fr5。Fr4 经硅胶柱色谱以二氯甲烷: 甲醇(10∶1 ~1∶1)洗脱,经 TLC 检识,相同点合并,再经反相硅胶柱色谱,以甲醇: 水(5% ~100%)梯度洗脱,结合重结晶得化合物 **1**(7.0 g)。Fr3 经硅胶柱色谱以二氯甲烷: 甲醇(20∶1 ~3∶1)洗脱,经 TLC 检识,相同点合并,再经反相硅胶柱(ODS)色谱,甲醇: 水(5% ~100%)梯度洗脱,得化合物 **2**(1.0 g),化合物 **3**(400 mg),化合物 **4**(700 mg)。Fr2 经硅胶柱色谱以二氯甲烷: 甲醇(30∶1 ~5∶1)洗脱,经 TLC 检识,相同点合并,再经 Sephadex LH-20 柱色谱以甲醇洗脱得化合物 **5**(40 mg),化合物 **6**(1.2 g),化合物 **7**(1.0 g)。Fr1 经硅胶柱色谱,二氯甲烷: 甲醇(40∶1 ~10∶1)洗脱,经 TLC 检识,相同点合并,再经 Sephadex LH-20 柱色谱以 70% 甲醇洗脱得化合物 **8**(70 mg)。

3　结构鉴定

化合物 1　白色结晶,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 2.03(3H,s,-$COCH_3$),2.97(1H,dd,J = 8.4,5.4 Hz,H-9),3.03(1H,td,J = 9.0,5.4 Hz,H-5),3.14-3.68(6H,m,sugar H),4.66(1H,dd,J = 14.4,1.2 Hz,H-10_a),4.62(1H,dd,J = 14.4,1.2 Hz,H-10_b),4.93(1H,d,J = 5.4 Hz,H-6),4.97(2H,dd,J = 7.8,5.4 Hz,H-1′),5.53(1H,d,J = 6.6 Hz,H-7),5.80(1H,s,H-1),7.37(1H,d,J = 1.8 Hz,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 93.0(C-1),150.5(C-3),106.4(C-4),37.5(C-5),85.9(C-6),128.9(C-7),144.5(C-8),45.4(C-9),62.3(C-10),171.8(C-11),171.3($COOCH_3$),100.3(C-1′),74.9(C-2′),79.2(C-3′),71.9(C-4′),78.4(C-5′),63.0(C-6′),22.4($COOCH_3$);ESI-MS: m/z 431.4 [M-H]$^-$。与文献[3]对照,鉴定为 6-*O*-乙酰鸡屎藤次苷。

化合物 2　白色结晶,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 2.59(1H,t,J = 8.4 Hz,H-9),3.05(1H,t,J = 6.0 Hz,H-5),3.25-3.42(5H,m,H-2′,3′,4′,5′,6a′),3.65(1H,dd,J = 12.0,5.4 Hz,H-6b′),3.77(3H,s,OCH_3),3.87(1H,m,H-6),4.24(1H,d,J = 15.6 Hz,H-10_a),4.48(1H,d,J = 15.6 Hz,H-10_b),4.74(1H,d,J = 7.5 Hz,H-1′),5.08(1H,d,J = 9.0 Hz,H-7),6.05(1H,d,J = 1.2 Hz,H-1),7.68(1H,s,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 100.1(C-1),154.0(C-3),106.9(C-4),41.3(C-5),74.0(C-6),128.4(C-7),150.1(C-8),44.5(C-9),60.3(C-10),168.0(C-11),99.1(C-1′),73.6(C-2′),77.1(C-3′),70.2(C-4′),76.4(C-5′),61.5(C-6′),50.4(OCH_3);ESI-MS: m/z 427 [M + Na]$^+$。与文献[4]对照,鉴定为 6α-羟基京尼平苷。

化合物 3　白色结晶,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 2.06(1H,dd,J = 15.6,5.4 Hz,H-6_a),2.70(1H,dd,J = 15.6,7.8 Hz,H-6_b),3.00(1H,m,H-9),3.05(2H,t,J = 8.4 Hz,H-5),3.13-3.67(6H,m,sugar H),3.99(1H,d,J = 14.4 Hz,H-10a),4.15(1H,d,J = 15.0 Hz,H-10b),4.54(1H,d,J = 7.8 Hz,H-1′),5.09(1H,d,J = 7.2 Hz,H-7),5.69(1H,br s,H-1),7.41(1H,s,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 96.2(C-1),151.5(C-3),112.1(C-4),35.2(C-5),38.6(C-6),126.0(C-7),144.6(C-8),46.3(C-9),59.9(C-10),168.6(C-11),99.0(C-1′),73.8(C-2′),77.7(C-3′),70.4(C-4′),77.1(C-5′),61.4(C-6′);ESI-MS: m/z 373.1 [M-H]$^-$。与文献[4]对照,鉴定为京尼平苷酸。

化合物 4　白色粉末,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 3.01(1H,m,H-9),3.06(1H,m,H-5),3.78(3H,s,OCH_3),3.23-3.89(6H,m,sugar H),4.21(1H,d,J = 15.6 Hz,H-10_a),4.36(1H,d,J = 15.6 Hz,H-10_b),4.57(1H,dt,J = 4.2,1.8 Hz,H-6),4.7(1H,d,J = 7.8 Hz,H-1′),5.22(1H,d,J = 6.6 Hz,H-7),5.83(1H,m,H-1),7.54(1H,d,J = 1.2 Hz,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 96.9(C-1),152.5(C-3),109.4(C-4),44.2(C-5),80.9(C-6),128.7(C-7),146.2(C-8),45.7(C-9),59.7(C-10),168.9(C-11),98.9(C-1′),73.4(C-2′),77.0(C-3′),70.1(C-4′),76.5(C-5′),61.3(C-6′),50.7(OCH_3);ESI-MS: m/z 427 [M + Na]$^+$。与文献[4]对照,鉴定为 6β-羟基京尼平苷。

化合物 5　白色结晶,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 2.12(3H,s,CH_3),2.67(1H,t,J = 8.4 Hz,H-9),3.06(1H,m,H-5),3.25-3.88(6H,m,sugar H),3.4(1H,m,H-6),3.77(3H,s,OCH_3),4.75(1H,d,J = 7.8 Hz,H-1′),4.82

~4.84(1H,m,H-10_a),4.97(1H,d,J = 15.0 Hz,H-10_b),5.09(1H,d,J = 9.0 Hz,H-7),6.05(1H,d,J = 1.2 Hz,H-1),7.68(1H,d,J = 1.2 Hz,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 99.9(C-1),154.0(C-3),106.7(C-4),41.0(C-5),74.0(C-6),130.4(C-7),144.6(C-8),44.9(C-9),62.4(C-10),167.9(C-11),99.2(C-1′),73.5(C-2′),77.2(C-3′),70.2(C-4′),76.5(C-5′),61.6(C-6′),19.4(CH_3),50.5(OCH_3),171.1($COOCH_3$);ESI-MS: m/z 445.1 [M-H]$^-$。与文献[5]对照,鉴定为交让木苷。

化合物 6 白色结晶,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 2.94(1H,t,J = 6.6 Hz,H-9),3.01(1H,t,J = 8.4 Hz,H-5),3.14(3H,s,OCH_3),3.18-3.65(6H,s,sugar H),4.01(1H,d,J = 16.2 Hz,H-10_a),4.26(1H,d,J = 5.4 Hz,H-6),4.29(1H,d,J = 16.2 Hz,H-10_b),4.58(1H,d,J = 7.8 Hz,H-1′),4.81(1H,d,J = 8.4 Hz,H-7),6.09(1H,s,H-1),7.5(1H,br.s,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 99.3(C-1),153.0(C-3),108.1(C-4),41.0(C-5),83.5(C-6),126.2(C-7),152.4(C-8),45.1(C-9),60.3(C-10),168.5(C-11),100.0(C-1′),73.9(C-2′),77.5(C-3′),70.3(C-4′),77.0(C-5′),61.2(C-6′),56.8(OCH_3);ESI-MS: m/z 403.1 [M-H]$^-$。与文献[6]对照,鉴定为6α-甲氧基京尼平苷酸。

化合物 7 白色结晶,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 2.98(1H,t,J = 7.8 Hz,H-9),3.05(1H,m,H-5),3.12(1H,m,H-6),3.15-3.67(6H,m,sugar H),4.00(1H,d,J = 15.0 Hz,H-10_a),4.13(1H,d,J = 15.0 Hz,H-10_b),4.50(1H,d,J = 7.8 Hz,H-1′),5.18(1H,d,J = 5.4 Hz,H-7),5.68(1H,s,H-1),7.39(1H,s,H-3)。^{13}C NMR(150 MHz,DMSO-d_6):δ 95.8(C-1),151.9(C-3),110.3(C-4),43.9(C-5),80.0(C-6),129.2(C-7),146.2(C-8),46.1(C-9),59.5(C-10),169.5(C-11),98.7(C-1′),73.7(C-2′),77.7(C-3′),70.4(C-4′),77.1(C-5′),61.5(C-6′);ESI-MS: m/z 389.3 [M-H]$^-$。与文献[7]对照,鉴定为去乙酰基车叶草苷酸。

化合物 8 黄色粉末,Molish 反应呈阳性。^{1}H NMR(600 MHz,DMSO-d_6):δ 3.27-4.57(6H,m,sugar H),3.57(1H,dt,J = 11.4 Hz,5.4 Hz,-CH_2OH),4.57(1H,dd,J = 11.4 Hz,4.8 Hz,-CH_2OH),5.12(1H,d,J = 7.2 Hz,H-1′),7.47(1H,s,H-4),7.93(2H,m,H-6,7),8.17(1H,dd,J = 6.0,3.0 Hz,H-5),8.22(1H,dd,J = 6.0,3.0 Hz,H-8),13.03(1H,br s,1-OH)。^{13}C NMR(150 MHz,DMSO-d_6):δ 162.5(C-1),124.1(C-2),162.4(C-3),106.8(C-4),135.4(C-4_a),127.4(C-5),133.3(C-6),133.3(C-7),127.0(C-8),133.2(C-8_a),187.6(C-9),111.8(C-9_a),181.9(C-10),134.2(C-10_a),101.3(C-1′),73.8(C-2′),77.8(C-3′),69.9(C-4′),76.5(C-5′),60.9(C-6′),51.4(CH_2OH);ESI-MS: m/z 431.1 [M-H]$^-$。与文献[8]对照,鉴定为光泽汀-3-*O*-葡萄糖苷。

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