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唐古特铁线莲化学成分研究

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摘 要: 利用硅胶、Sephadex LH-20、ODS、MPLC 柱色谱等方法对唐古特铁线莲的化学成分进行分离纯化,根据理化性质及波谱数据鉴定化合物的结构。从唐古特铁线莲乙酸乙酯萃取部位分离鉴定了 11 个化合物,分别鉴定为木犀草素(1),Clemaphenol A(2),α-亚麻酸(3),胡萝卜苷(4),胡萝卜苷苷元(5),常春藤-3-*O*-α-L-鼠李糖(1→4)-β-D-葡萄糖(6),常春藤-3-*O*-α-L-阿拉伯糖(1→3)-α-L-鼠李糖(1→4)-β-D-葡萄糖(7),Acanjaposide G(8),常春藤配基(9),芹菜素(10),灯台酸(11)。所有化合物均为首次从唐古特铁线莲中分离得到。

关键词: 唐古特铁线莲;化学成分;三萜皂苷;结构鉴定

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Chemical Constituents of *Clematis tangutica*

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Abstract: The chemical constituents of *Clematis tangutica* was investigated by the methods of Si-gel,Sephadex LH-20,ODS and MPLC,and the structures of compounds were identified by means of physicochemical properties and spectral analysis. Eleven compounds were isolated from the ethyl acetate fraction of *Clematis tangutica*,and identified as luteolin(**1**),clemaphenol A(**2**),alpha-linolenic acid(**3**),daucosterol(**4**),daucosterolaglycone(**5**),hederagenin-3-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(**6**),hederagenin-3-*O*-α-L-arabinopyranosyl(1→3)-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(**7**),Acanjaposide G(**8**),hederagenin(**9**),apigenin(**10**),echitin(**11**). All of these compounds were obtained from the plant for the first time.

Key words: *Clematis tangutica*; chemical constituents; triterpenoidsaponin; structure identification

唐古特铁线莲(*Clematis tangutica*(Maxim.)Korsh)为毛茛科铁线莲属植物,其性辛、甘、温,具有祛寒,增生胃火,活血化淤,排脓散痈,消痞块的作用。常用于胃寒,消化不良,痞瘤病,黄水病及寒性肿瘤,浮肿等症的治疗[1]。铁线莲属植物主要的化学成分为三萜皂苷类化合物,现代药理研究表明铁线莲属植物的皂苷类化合物具有抗肿瘤、抗炎、镇痛等药理活性[2-3]。关于唐古特铁线莲化学成分的报道较少[4],且报道的多为三萜皂苷类化合物,对唐古特铁线莲进行系统的化学成分研究是十分必要的,能为其资源的开发利用提供理论基础。

1 材料、仪器与试剂

1.1 材料

唐古特铁线莲(*Clematis tangutica*(Maxim.)Korsh)采自青海门源仙米林场,经中国科学院藏药研究重点实验室高级工程师梅丽娟鉴定为毛茛科铁线莲属植物唐古特铁线莲(*Clematis tangutica*(Maxim.)Korsh)。

柱层析硅胶(200~300 目),TLC 硅胶(GF_{254},化学纯)均为青岛海洋化工厂产品;葡聚糖凝胶 Sephadex LH-20,Pharmacia 公司产品;RP-18 硅胶(40~60 μm),德国 Amersham Biosciences 公司产品。

1.2 仪器

RE-52A 型旋转蒸发器;DZKW-C 型电子恒温水浴锅;KQ-250DB 型超声波清洗器;DZF-6050 型恒温干燥箱;AG-204 型万分之一分析天平(METTLER 公司);SHB-Ⅲ型循环水真空泵;核磁共振测定:Bruker AM400 和 Varian Mercury 400BB 型超导核磁共振

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仪; HanBang-NP-7000C 型中压制备,汉邦科技有限公司产品; Agilents 1200 型液相色谱仪,美国安捷伦仪器有限公司。

1.3 试剂

实验所用石油醚,氯仿,乙酸乙酯,正丁醇,甲醇,乙醇,丙酮均为分析纯,TLC 显色剂为 5% 硫酸乙醇,L-B 反应试剂,Molish 反应试剂

2 提取与分离

干燥唐古特铁线莲全草粗粉共 5 kg。用纱布包裹置于提取容器内,8 倍量 90% 乙醇冷浸 12 h 后,在沸水浴中回流提取 2 次,每次 2 h。合并提取液,过滤,减压浓缩,回收乙醇,得醇提物浸膏。将醇提物浸膏分散于适量水中,分别用石油醚、乙酸乙酯、正丁醇萃取。乙酸乙酯部分采用硅胶柱层析,氯仿-丙酮体系 20∶1、15∶1、10∶1、5∶1、1∶1 依次洗脱,最后甲醇冲柱,每 500mL 洗脱液收集一次,用 TLC 检测,合并为 9 个组分。经反复正相硅胶柱色谱,并通过反相 ODS,Sephadex LH-20 凝胶色谱,中压液相制备(MPLC)等方法从中分离得到化合物 **1** ~ **11**。

3 结构鉴定

化合物 1 黄色针晶。^{1}H NMR(400 MHz,DMSO-d_6) δ: 12.97(1H,s,5-OH),7.41(1H,d,J = 8 Hz,H-6′),7.39(1H,s,H-2′),6.89(1H,d,J = 8 Hz,H-5′),6.87(1H,s,H-8),6.43(1H,s,H-3),6.17(1H,s,H-6)。^{13}C NMR(100 MHz,DMSO-d_6) δ: 181.7(C-4),164.2(C-2),163.9(C-7),161.5(C-5),157.3(C-9),149.7(C-4′),145.7(C-3′),121.5(C-1′),119.0(C-6′),116.0(C-5′),113.4(C-2′),103.7(C-10),102.9(C-3),98.8(C-6),93.9(C-8)。^{13}C NMR 及 ^{1}H NMR 波谱数据与文献[9] 报道的木犀草素数据基本一致,因此化合物 **1** 鉴定为木犀草素

化合物 2 无色油状液体,EI-MS m/z: 358(M^+)。^{1}H NMR(400 MHz,CD_3Cl) δ: 3.10(m,H-1,H-5),4.73(d,J = 4 Hz,H-2,H-6),3.85(dd,J = 8.5,3.1 Hz,H-4,H-8),4.23(dd,J = 8.5,6.3 Hz,H-4,8),6.86(br,s,H-2,2"),6.88(d,J = 8 Hz,H-5,5"),6.82(dd,J = 8,1.1 Hz,H-6,6"),3.87(s,-OCH_3),5.61(br,-OH)。^{13}C NMR(100 MHz,CD_3Cl) δ: 54.09(C-1,5),85.9(C-2,6),71.6(C-4,8),132.8(C-1′,1"),108.6(C-2′,2"),145.2(C-3′,3"),146.7(C-4′,4"),114.3(C-5′,5"),118.9(C-6′,6"),55.9(-OCH_3)。^{13}C NMR 及 ^{1}H NMR 波谱数据与文献[10] 报道的 Clemaphenol A 数据基本一致,因此化合物 **2** 鉴定为 Clemaphenol A。

化合物 3 淡黄色油状物,$C_{18}H_{30}O_2$; ESI-MS m/z: 395 $[M-H]^-$。^{1}H NMR(600 MHz,CD_3Cl) δ: 5.28-5.41(6H,m,H-9,10,12,13,15,16),2.81(4H,t,J = 5.5 Hz,H-11,14),2.34(2H,t,J = 7.5 Hz),2.08(4H,m,H-8,17),1.62(2H,m,H-3),1.25-1.31(8H,m,H-4,5,6,7),0.97(3H,t,J = 7.5 Hz,H-18). 氢谱数据与文献[11] 报道一致; 与 α-亚麻酸对照品在三种系统下 TLC 共薄层,R_f 值相同,表明该化合物是 α-亚麻酸。

化合物 4 白色粉末,mp. 276 ~ 278 ℃,EI-MS m/z: 576(M +)。Liebermann-Burchard 反应阳性,Molish 反应阳性。^{1}H NMR(DMSO-d_6,600 MHz) δ: 5.32(1H,d,J = 4.8 Hz,H-6),4.21(1H,d,J = 7.8 Hz,H-1′),3.13(1H,q,J = 4.8 Hz,H-4′),3.05(2H,q,J = 5.2 Hz,H-3′,2′),2.90(1H,m,H-5′),3.33(1H,dd,J = 5.4,10.8 Hz,H-6′),3.125(2H,m,H-6′),3.55(1H,m,H-3α); 0.85,1.07(each 3H,s,2 × CH_3)。^{13}C NMR(DMSO-d_6,150 MHz) δ: 37.4(C-1),32.4(C-2),79.5(C-3),42.6(C-4),140.9(C-5),122.4(C-6),32.4(C-7),32.3(C-8),50.7(C-9),36.6(C-10),21.6(C-11),39.1(-12),42.6(C-13),57.3(C-14),23.5(C-15),28.7(C-16),56.6(C-17),11.6(C-18),19.6(C-19),36.7(C-20),19.2(C-21),34.5(C-22),26.6(C-23),46.3(C-24),29.6(C-25),19.6(C-26),19.3(C-27),23.1(C-28),12.2(C-29),101.7(C-1′),74.1(C-2′),76.5(C-3′),70.8(C-4′),77.1(C-5′),62.1(C-6′)。其 ^{13}C NMR 和 ^{1}H NMR 数据与文献[12] 报道的胡萝卜苷数据基本一致,因此,化合物 **4** 鉴定为胡萝卜苷。

化合物 5 白色粉末,易溶于氯仿。^{1}H NMR(CD_3Cl,600 MHz) δ: 7.26(1H,s,3-OH),5.35(1H,d,J = 4.8 Hz),1.01(6H,s,26,27-CH_3),0.91(3H,s,18-CH_3),0.93(3H,s,19-CH_3); ^{13}C NMR(CD_3Cl,150 MHz) δ: 37.3(C-1),31.9(C-2),71.8(C-3),42.3(C-4),140.7(C-5),121.7(C-6),32.3(C-7),33.0(C-8),50.1(C-9),36.5(C-10),21.1(C-11),39.8(C-12),42.3(C-13),56.9(C-14),23.1(C-15),28.2(C-16),56.7(C-17),11.8(C-18),19.8(C-19),36.7(C-20),19.0(C-21),34.4(C-22),

26.1(C-23),45.8(C-26),19.4(C-27),23.3(C-28),11.9(C-29)。**其波谱数据与文献[12]中报道的胡萝卜苷苷元的数据相比,除** C-3 δ_C **相差** 8 ppm(**苷化位移**)**外,其他数据基本一致,因此化合物 5 鉴定为胡萝卜苷苷元。**

化合物 6 白色粉末, mp. 218 ~ 220 ℃,^{1}H NMR(DMSO-d_6,600 MHz) δ: 0.52,0.67,0.83,0.93,1.02,1.05(each 3H,6 × CH_3),4.28(1H,d,J = 6 Hz,H-1 of Glc),5.11(1H,s,H-1 of Rha);^{13}C NMR(DMSO-d_6,150 MHz) δ: 38.1(C-1),27.2(C-2),79.2(C-3),42.2(C-4),47.1(C-5),17.7(C-6),32.8(C-7),39.2(C-8),47.3(C-9),38.1(C-10),23.3(C-11),121.5(C-12),143.8(C-13),41.3(C-14),27.1(C-15),23.3(C-16),46.1(C-17),41.3(C-18),47.1(C-19),30.3(C-20),32.8(C-21),35.9(C-22),68.1(C-23),12.9(C-24),15.5(C-25),17.7(C-26),25.5(C-27),178.5(C-28),32.8(C-29),22.8(C-30);3-*O*-Rha: 99.8(C-1′),70.4(C-2′),72.0(C-3′),74.2(C-4′),68.1(C-5′),17.7(C-6′);-Glc: 102.9(C-1″),74.2(C-2″),79.2(C-3″),79.3(C-4″),79.8(C-5″),64.3(C-6″)。**其波谱数据与文献[13]中报道的常春藤-3-*O*-α-L-鼠李糖(1→4)-β-D-葡萄糖数据基本一致。因此,化合物 6 鉴定为常春藤-3-*O*-α-L-鼠李糖(1→4)-β-D-葡萄糖。**

化合物 7 白色粉末,^{1}H NMR(DMSO-d_6,600 MHz) δ: 5.12(1H,brs,12-H),0.60,0.83,0.93,1.05,1.08,1.24(each 3H,6 × CH_3);^{13}C NMR(DMSO-d_6,150 MHz) δ: 38.1(C-1),27.2(C-2),79.3(C-3),42.2(C-4),47.1(C-5),17.8(C-6),32.8(C-7),39.1(C-8),47.1(C-9),38.2(C-10),23.3(C-11),121.5(C-12),143.8(C-13),41.3(C-14),27.1(C-15),23.3(C-16),46.1(C-17),41.3(C-18),47.1(C-19),30.3(C-20),32.8(C-21),35.9(C-22),68.1(C-23),13.0(C-24),15.5(C-25),17.7(C-26),25.5(C-27),178.5(C-28),32.8(C-29),22.6(C-30);3-*O*-Ara: 99.7(C-1′),75.7(C-2′),73.9(C-3′),69.4(C-4′),64.9(C-5′);-Rha: 103.1(C-1″),70.8(C-2″),71.1(C-3″),73.9(C-4″),68.1(C-5″),17.1(C-6″);-Glc: 101.9(C-1‴),74.2(C-2‴),79.3(C-3‴),79.3(C-4‴),79.2(C-5‴),64.9(C-6‴)。**其波谱数据与化合物 6 基本一致,比化合物 6 多了一个阿拉伯糖。因此,化合物 7 鉴定为常春藤-3-*O*-α-L 阿拉伯糖(1→3)-α-L-鼠李糖(1→4)-β-D-葡萄糖。**

化合物 8 白色粉末。^{13}C NMR(DMSO-d_6,150 MHz) δ: 39.0(C-1),27.1(C-2),75.9(C-3),57.7(C-4),49.7(C-5),20.5(C-6),33.0(C-7),40.7(C-8),48.1(C-9),36.1(C-10),24.7(C-11),122.7(C-12),144.1(C-13),41.4(C-14),28.2(C-15),24.7(C-16),48.1(C-17),41.4(C-18),46.2(C-19),30.1(C-20),33.9(C-21),31.7(C-22),180.7(C-23),12.3(C-24),16.6(C-25),17.8(C-26),26.0(C-27),176.6(C-28),33.0(C-29),24.7(C-30);28-*O*-Glc: 95.6(C-1′),73.3(C-2′),77.9(C-3′),70.9(C-4′),70.9(C-5′),70.1(C-6′);-Rha: 103.7(C-1″),72.5(C-2″),72.1(C-3″),73.2(C-4″),70.8(C-5″),18.9(C-6″);-Glc: 106.7(C-1‴),75.9(C-2‴),77.9(C-3‴),78.3(C-4‴),77.1(C-5‴),63.1(C-6‴)。**其波谱数据与文献[14]中报道的** Acanjaposide G **基本一致,因此,化合物 8 鉴定为** Acanjaposide G。

化合物 9 白色结晶, mp. 330 ~ 332 ℃。^{1}H NMR(DMSO-d_6,600 MHz) δ: 5.38(1H,brs,12-H),4.14(1H,m,3-H),4.14,4.38(each 1H,d,J = 10 Hz,23-H_2),1.24,1.08,1.04,1.01,0.98,0.89(each 3H,6 × CH_3);^{13}C NMR(DMSO-d_6,150 MHz) δ: 38.8(C-1),27.1(C-2),72.9(C-3),41.7(C-4),47.4(C-5),17.0(C-6),33.3(C-7),39.8(C-8),47.0(C-9),37.8(C-10),23.3(C-11),121.5(C-12),143.8(C-13),41.7(C-14),28.7(C-15),23.3(C-16),46.4(C-17),41.7(C-18),46.1(C-19),30.3(C-20),33.2(C-21),32.7(C-22),67.0(C-23),12.5(C-24),15.4(C-25),17.4(C-26),26.4(C-27),178.4(C-28),33.2(C-29),23.8(C-30)。**其波谱数据与文献[15]中报道的常春藤配基数据基本一致,因此,化合物 9 鉴定为常春藤配基。**

化合物 10 黄色针状结晶(甲醇),ESI-MS m/z: 269 $[M-H]^-$,mp. 340 ~ 343 ℃。^{1}H NMR(DMSO-d_6,600 MHz) δ: 12.95(1H,s,C_5-OH),10.78(1H,C_7-OH),9.91(1H,s,$C_{4'}$-OH),7.92(2H,d,J = 8.4 Hz,H-2′,6′),6.91(2H,d,J = 8.4 Hz,H-3′,5′),6.78(1H,s,H-3),6.47(1H,d,J = 2.4 Hz,H-8),6.18(1H,d,J = 2.4 Hz,H-6);^{13}C NMR(DMSO-d_6,150 MHz) δ: 164.0(C-2),103.6(C-3),181.6(C-4),158.2(C-5),98.8(C-6),163.7(C-7),93.9(C-8),

161.1(C-9),102.8(C-10),121.1(C-1′),128.4(C-2′),115.9(C-3′),161.2(C-4′),116.5(C-5′),128.2(C-6′)。**以上数据与文献[16]中报道的芹菜素波谱数据基本一致,因此化合物10鉴定为芹菜素。**

化合物11 黄色粉末,mp. 245 ~ 248 ℃,EI-MS *m/z*: 578 [M]$^+$。^{1}H NMR(DMSO-d_6,600 MHz) δ: 6.85(1H,s,H-3),6.46(1H,d,*J* = 2.4,H-6),6.79(1H,d,*J* = 2.4,H-8),7.48(1H,d,*J* = 16.2,H-12),6.32(1H,d,*J* = 16.2,H-13),6.91(2H,d,*J* = 9.0,H-15,19),7.35(4H,d,*J* = 9.0,H-16,18,3′,5′),7.93(2H,d,*J* = 9.0,H-2′,6′),5.15(1H,d,*J* = 7.8,H-Glc-1);^{13}C NMR(DMSO-d_6,150 MHz) δ: 164.1(C-2),102.9(C-3),181.8(C-4),161.3(C-5),99.4(C-6),162.6(C-7),94.6(C-8),156.8(C-9),105.3(C-10),166.3(C-11),113.6(C-12),144.8(C-13),124.8(C-14),130.0(C-15),115.6(C-16),161.0(C-17),115.5(C-18),130.6(C-19),120.8(C-1′),128.4(C-2′),115.9(C-3′,5′),161.0(C-4′),129.9(C-6′); 7-*O*-Glc: 99.4(C-1″),72.8(C-2″),73.7(C-3″),69.9(C-4″),76.1(C-5″),63.3(C-6″)。**其数据与文献[17]报道的灯台酸波谱数据基本一致,因此,化合物11鉴定为灯台酸。**

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