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巴天酸模的化学成分

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摘　要:采用多种色谱手段从羊蹄类中药巴天酸模(*Rumex patientia* L.)乙酸乙酯部位分到 12 个化合物,波谱学方法鉴定了它们的结构,分别为 2,4-二羟基-3,6-二甲基苯甲酸乙酯(**1**),1-(2,4-Dihydroxy-6-methyl phenyl)-acetophenone(**2**),大黄素(**3**),大黄酚(**4**),槲皮苷(**5**),Imperanene(**6**),2,3-Dihydro-2-(4-hydroxy-3,5-dimethoxyphenyl)-3-hydroxymethyl-5-(2-formylvinyl)-7-methoxybenzofuran(**7**),4-酮松脂酚(**8**),(+)-Lyoniresinol 3α-*O*-β-D-glucopyranoside(**9**),乌苏酸(**10**),5-烯-7α-羟基谷甾醇(**11**)和 β-谷甾醇(**12**)。其中化合物 **1**,**2**,**5**~**11** 均为首次从该中药中分离得到。

关键词:巴天酸模;蓼科;化学成分

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Compounds from the Aerial Parts of *Rumex patientia*

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Abstract:Twelve compounds were isolated from the aerial parts of *Rumex patientia*. Their structures were identified as Methyl 2,4-dihydroxy-3,6-dimethylbenzoate(**1**),1-(2,4-Dihydroxy-6-methyl phenyl)-acetophenone(**2**),Emodin(**3**),Chrysophanol(**4**),Quercitrin(**5**),Imperanene(**6**),2,3-Dihydro-2-(4-hydroxy-3,5-dimethoxyphenyl)-3-hydroxymethyl-5-(2-formylvinyl)-7-methoxybenzofuran(**7**),4-Ketopinoresinol(**8**),(+)-Lyoniresinol 3α-*O*-β-D-glucopyranoside(**9**),Ursolic acid(**10**),5-en-7α-Hydroxysitosterol(**11**),and β-stiosterol(**12**),respectively,by spectroscopic methods. Among these,compounds **1**,**2**,**5-11** were isolated from this plant for the first time.

Key words:*Rumex patientia* L.;polygonaceae;chemical constituents

巴天酸模(*Rumex patientia* L.)属蓼科酸模属植物,广泛分布于我国长江以北地区,以根入药,俗称为羊蹄,为常用草药[1]。现代药理研究表明其具有较好的生物活性,具较强的抗结核、抗肿瘤及抗炎活性[2,3]。报道称其嫩茎和叶中含有丰富的营养物质,可作为优良的饲用牧草[4]。近年来药学界对其药用部位根的研究报道较多,但是其地上部分是否具有较好的药用前景还需要研究。我们对其地上部分的化学成分研究,从中分离鉴定了 12 个化合物,其中 9 个为本种首次分离。

1　仪器、试剂和材料

VGAUTO Spec-3000 及 Finnigan MAT 90 质谱仪;Bruker AM-400 及 DRX-500 MHz 核磁共振仪(TMS 作为内标,δ 为 ppm,*J* 为 Hz)等。硅胶(80(100 目)和层析用硅胶(200~300 目),青岛海洋化工厂生产;RP-18(40~60 m),由 Merck 公司生产;MCI gel CHP 20P 系日本三菱公司产品;Sephadex LH-20 为 GE 公司产品。显色剂为 10% H_2SO_4 乙醇溶液,试剂均为工业级重蒸后用。巴天酸模样品 2009 年采自甘肃省,由中国科学院昆明植物研究所彭华研究员鉴定为为蓼科酸模属巴天酸模。

2　提取与分离

巴天酸模地上部分(13 kg),采用 80% 工业乙醇回流提取提取 3 次(2、2、1 h),合并提取液浓缩至无醇味,加适量水使其分散于水中,依次用等体积石油醚、乙酸乙酯、正丁醇各萃取 3 次,分别得石油醚萃取部位(100 g),乙酸乙酯萃取部位(150 g)和正丁醇萃取部位(95 g)。取乙酸乙酯部位浸膏,拌样

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后用氯仿-甲醇系统梯度洗脱,得 8 个组分。组份 B 依次经 Sephadex LH-20、硅胶柱层析得化合物 **3**;组份 D 依次经 Sephadex LH-20,硅胶柱层析得化合物 **1**,**2**,**8**,**10** 和 **12**;组份 F 经 MCI gel CHP 20P 柱,以甲醇:水(10%)梯度洗脱,再经 RP-18 柱,以甲醇:水(40%)洗脱得化合物 **7**,**11**;组份 G 经 MCI gel CHP 20P 柱,以甲醇(水(10%)梯度洗脱,再经 RP-18 柱,以甲醇:水(50%)梯度洗脱得化合物 **4**,**5**,**6** 和 **9**。

3 结构鉴定

化合物 1 白色粉末。^{1}H NMR (400 MHz, pyridine-d_5) δ:12.67 (1H, s, OH), 6.66 (1H, s, H-5), 4.27 (2H, q, J = 7.0 Hz, H-1′), 1.19 (3H, t, J = 7.0 Hz, H-2′), 2.52 (3H, s, 3-CH_3), 2.50 (3H, s, 6-CH_3); ^{13}C NMR (100 MHz, pyridine-d_5) δ:172.7 (C-7), 164.0 (C-2), 161.9 (C-4), 140.3 (C-6), 111.6 (C-5), 109.8 (C-3), 104.6 (C-1), 61.3 (C-1′), 24.5 (6-CH_3), 14.2 (C-2′), 18.7 (3-CH_3)。以上数据和文献数据基本一致[5],故确定化合物 **1** 为 2,4-二羟基-3,6-二甲基苯甲酸乙酯。

化合物 2 淡黄色固体。^{1}H NMR (500 MHz, acetone-d_6) δ:2.60 (3H, s, 1-$COCH_3$), 6.29 (1H, J = 2.4 Hz, H-3), 6.20 (1H, d, J = 2.4 Hz, H-5), 2.52 (3H, s, 6-CH_3); ^{13}C NMR (125 MHz, acetone-d_6) δ: 33.1 (1-$COCH_3$), 204.8 (1-$COCH_3$), 166.9 (C-4), 163.3 (C-2), 143.6 (C-6), 116.2 (C-1), 112.5 (C-5), 101.8 (C-3), 24.5 (6-CH_3)。以上数据和文献数据基本一致[6],故确定化合物 **2** 为 1-(2,4-dihydroxy-6-methyl phenyl)-acetophenone。

化合物 3 橙红色针晶。^{1}H NMR (500 MHz, DMSO-d_6) δ:2.44 (3H, s, 3-CH_3), 7.52 (1H, brs, H-4), 7.22 (1H, d, J = 2.15 Hz, H-5), 7.10 (1H, brs, H-2), 6.63 (1H, d, J = 2.15 Hz, H-7), 12.03 (1H, brs, 8-OH), 12.16 (1H, brs, 1-OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 191.7 (C-9), 182.1 (C-10), 166.4 (C-6), 166.2 (C-8), 163.2 (C-1), 149.5 (C-3), 136.6 (C-5a), 134.2 (C-4a), 124.9 (C-2), 121.4 (C-4), 114.4 (C-1a), 111.0 (C-8a), 109.7 (C-5), 108.8 (C-7), 22.0 (3-CH_3)。以上数据和文献数据基本一致[7],故确定化合物 **3** 为大黄素。

化合物 4 淡黄色针晶。^{1}H NMR (500 MHz, DMSO-d_6) δ:7.69 (1H, d, J = 8.0 Hz, H-5), 7.79 (1H, t, J = 8.0, 7.4 Hz, H-6), 7.53 (1H, s, H-4), 7.36 (1H, d, J = 7.4 Hz, H-7), 7.20 (1H, s, H-2), 2.42 (3H, s, 3-CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 191.8 (C-9), 181.8 (C-10), 161.7 (C-8), 161.4 (C-1), 149.4 (C-3), 137.6 (C-6), 133.5 (C-5a), 133.2 (C-4a), 124.7 (C-2), 124.3 (C-7), 120.8 (C-5), 119.5 (C-4), 113.9 (C-1a), 116.0 (C-8a), 21.8 (3-CH_3)。以上数据和文献数据基本一致[7],故确定化合物 **4** 为大黄酚。

化合物 5 黄色针晶。^{1}H NMR (500 MHz, pyridine-d_5) δ:7.99 (1H, d, J = 2.0 Hz, H-2′), 7.67 (1H, dd, J = 8.3, 2.0 Hz, H-6′), 7.33 (1H, d, J = 8.3 Hz, H-5′), 6.68 (1H, d, J = 2.0 Hz, H-8), 6.65 (1H, d, J = 2.0 Hz, H-6), 6.17 (1H, br. s, H-1"), 5.07 (1H, d, J = 1.4 Hz, H-2"), 4.65 (1H, dd, J = 9.1, 3.2 Hz, H-3"), 4.37 (4.24 (2H, m, H-4", H-5"), 1.42 (3H, d, J = 5.9 Hz, H-6"); ^{13}C NMR (125 MHz, pyridine-d_5) δ: 178.7 (C-4), 165.5 (C-7), 162.5 (C-5), 157.9 (C-2), 157.3 (C-9), 150.2 (C-4′), 146.8 (C-3′), 122.0 (C-1′), 121.9 (C-6′), 116.8 (C-2′), 116.2 (C-5′), 105.1 (C-10), 103.7 (C-1"), 99.5 (C-6), 94.3 (C-8), 73.0 (C-4"), 72.2 (C-2"), 71.8 (C-3"), 71.7 (C-5"), 18.1 (C-6")。以上数据和文献数据基本一致[8],故确定化合物 **5** 为槲皮苷。

化合物 6 白色固体。^{1}H NMR (500 MHz, methanol-d_4) δ: 2.53 (2H, overlap, H-9, H-10a), 2.76 (1H, dd, J = 12.7, 5.2 Hz, H-10b), 3.53 (2H, J = 5.7, 2.9 Hz, H-11), 3.73 (3H, s, OMe), 3.81 (3H, s, OMe), 5.92 (1H, dd, J = 15.9, 8.2 Hz, H-8), 6.18 (1H, d, J = 15.9 Hz, H-7), 6.59 (1H, dd, J = 8.0, 1.7 Hz, Ar-H), 6.66 (2H, overlap, Ar-H), 6.73 (2H, overlap, Ar-H), 6.89 (1H, J = 1.5 Hz, Ar-H); ^{13}C NMR (125 MHz, methanol-d_4) δ:149.0 (C-16) 148.6 (C-3), 147.1 (C-4), 145.6 (C-15), 133.2 (C-7), 132.5 (C-12), 131.5 (C-1), 129.9 (C-8), 123.0 (C-17), 120.5 (C-2), 116.2 (C-14), 115.9 (C-5), 114.4 (C-13), 110.4 (C-6), 66.1 (C-11), 56.4 (2 × OMe), 49.0 (C-9), 38.7 (C-10)。以上数据和文献数据基本一致[9],故确定化合物 **6** 为 imperanene。

化合物 7 淡黄色胶状。^{1}H NMR (500 MHz, pyridine-d_5) δ:11.01 (1H, br. s, 4′-OH), 9.82 (1H, d, J = 7.5 Hz, H-10), 7.19 (2H, s, H-2′, H-6′), 7.09 (2H, s, H-4, H-6), 7.54 (1H, d, J = 15.0 Hz, H-8), 6.89 (1H, dd, J = 15.0, 7.5 Hz, H-9), 6.17 (1H, d, J = 7.8 Hz, H-2), 4.30 (2H, d, J = 5.3 Hz, H-3a), 3.85 (3H, s, 7-OMe), 3.72 (6H, s, 3′, 5′-OMe), 3.70 (1H, m, H-3); ^{13}C NMR (125 MHz, pyridine-d_5) δ:193.5 (C-10), 153.6 (C-8), 152.3 (C-7a), 149.4 (C-3′, C-5′), 145.2 (C-7), 138.0 (C-4′), 135.3 (C-1′), 131.8 (C-4a), 131.5 (C-5), 128.6 (C-9), 119.3 (C-4), 113.6 (C-6), 105.0 (C-2′, C-6′), 90.0 (C-2), 63.8 (C-3a), 56.4 (3′, 5′-OMe), 56.2 (7-OMe), 54.2 (C-3)。以上数据和文献数据基本一致[10],故确定化合物 **7** 为 2,3-dihydro-2-(4′-hydroxy-3′, 5-dimethoxyphenyl)-3-hydroxymethyl-5-(2-formylvinyl)-7-methoxybenzofuran。

化合物 8 白色固体。^{1}H NMR (500 MHz, acetone-d_6) δ:6.96 (1H, d, J = 1.7 Hz, H-2"), 6.81 (6.89 (4H, m, H-5′, H-6′, H-5", H-6"), 5.20 (1H, d, J = 2.4 Hz, H-3), 3.48 (1H, m, H-4), 3.82 (3H, s, 3"-OCH_3), 6.97 (1H, d, J = 1.6 Hz, H-2′), 5.79 (1H, d, J = 6.1 Hz, H-7), 3.65 (1H, m, H-8), 3.77 (1H, dd, J = 9.7, 7.3 Hz, H-1a), 3.65 (1H, dd, J = 9.7, 4.8 Hz, H-1b), 3.84 (3H, s, 3′-OCH_3); ^{13}C NMR (125 MHz, acetone-d_6) δ:177.9 (C-5), 148.4 (C-3′), 147.0 (C-4′), 147.6 (C-3"), 146.9 (C-4"), 133.2 (C-1"), 129.0 (C-1′), 119.1 (C-6′), 118.4 (C-6"), 115.8 (C-5′), 115.6 (C-5"), 109.2 (C-2′), 109.2 (C-2"), 84.1 (C-3), 86.4 (C-7), 73.8 (C-1), 56.2 (3′-OCH_3), 56.1 (3"-OCH_3), 55.2 (C-4), 54.9 (C-8)。以上数据和文献数据基本一致[11],故确定化合物 **8** 为 4-ketopinoresinol。

化合物 9 白色粉末。^{1}H NMR (500 MHz, methanol-d_4) δ:6.36 (2H, s, H-2′, H-6′), 6.51 (1H, s, H-8), 4.35 (1H, d, J = 6.6 Hz, H-3a), 4.21 (1H, d, J = 6.6 Hz, H-3a), 3.83 (1H, dd, J = 9.8, 5.4 Hz, H-4), 3.48 (1H, dd, J = 10.9, 6.6 Hz, H-2a), 3.38 (1H, dd, J = 10.9, 6.6 Hz, H-2a), 2.65 (1H, dd, J = 14.9, 5.4 Hz, H-1a), 2.55 (1H, dd, J = 14.9, 11.7 Hz, H-1b), (1.96 (1H, m, H-3), (1,59 (1H, m, H-2), 3,79 (3H, s, OCH_3), 3.26 (3H, s, OCH_3), 3.68 (6H, s, 2 × OCH_3); ^{13}C NMR (125 MHz, methanol-d_4) δ:33.9 (C-1), 149.0 (C-3′), 149.0 (C-5′), 148.6 (C-5), 147.6 (C-7), 139.4 (C-1′), 138.9 (C-6), 134.4 (C-4′), 130.1 (C-9), 126.4 (C-10), 107.7 (C-8), 106.7 (C-6′), 106.7 (C-2′), 104.9 (C-1"), 78.2 (C-5"), 78.0 (C-3"), 75.2 (C-2"), 71.6 (C-4"), 71.2 (C-3a), 66.1 (C-2a), 62.8 (C-6"), 60.1 (5-OCH_3), 56.8 (3′-OCH_3), 56.8 (5′-OCH_3), 56.5 (7-OCH_3), 46.7 (C-3), 42.8 (C-4), 40.5 (C-2)。以上数据和文献数据基本一致[12],故确定化合物 **9** 为(+)-lyoniresinol 3α-*O*-β-D-glucopyranoside。

化合物 10 白色粉末。^{1}H NMR (400 MHz, pyridine-d_5) δ:5.49 (1H, t, J = 3.6 Hz, H-12), 2.63 (1H, d, J = 10.9 Hz, H-18), 1.24 (3H, s, H-27), 1.23 (3H, s, H-23), 1.05 (3H, s, H-25), 1.02 (3H, s, H-24), 1.00 (3H, d, J = 6.1 Hz, H-29), 0.94 (3H, d, J = 6.1 Hz, H-30), 0.87 (3H, s, H-26), 3.44 (1H, dd, J = 10.38, 6.10 Hz, H-3), 2.33 (1H, td, J = 13.4, 4.7 Hz, H-2a), 2.11 (1H, td, J = 13.4, 4.3 Hz, H-2b); ^{13}C NMR (100 MHz, pyridine-d_5) δ:179.9 (C-28), 139.8 (C-13), 125.7 (C-12), 55.9 (C-5), 78.3 (C-3), 53.2 (C-18), 48.1 (C-9), 48.1 (C-17), 42.6 (C-14), 40.0 (C-8), 39.6 (C-4), 39.5 (C-20), 39.4 (C-19), 39.0 (C-1), 37.5 (C-22), 37.0 (C-10), 33.9 (C-7), 31.4 (C-21), 28.8 (C-23), 28.6 (C-15), 28.2 (C-2), 25.0 (C-16), 24.0 (C-11), 23.8 (C-27), 21.5 (C-30), 18.8 (C-6), 17.5 (C-26), 17.5 (C-29), 16.6 (C-25), 15.5 (C-24)。以上数据和文献数据基本一致[13],故确定化合物 **10** 为乌苏酸。

化合物 11 白色固体。^{1}H NMR (500 MHz, DMSO-d_6) δ:5.39 (lH, d, J = 5.1 Hz, H-6), 3.26 (1H, m, H-3), 3.60 (1H, m, H-7), 0.61 (3H, s, H-18), 0.88 (3H, d, J = 6.6 Hz, H-21), 0.80 (3H, d, J = 6.6 Hz, H-26), 0.74 (3H, d, J = 6.6 Hz, H-27), 0.81 (3H, d, J = 7.3 Hz, H-29), 4.72 (lH, d, J = 5.14 Hz, 7-OH), 4.07 (lH, d, J = 6.60 Hz, 3-OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ:143.7 (C-5), 124.7 (C-6), 69.9 (C-3), 63.4 (C-7), 55.5 (C-17), 49.1 (C-14), 45.2 (C-24), 42.1 (C-4), 41.6 (C-13), 41.4 (C-9), 39.1 (C-12), 37.4 (C-8), 36.7 (C-1), 36.6 (C-10), 35.6 (C-20), 33.4

(C-22),31.3 (C-2),28.8 (C-25),28.0 (C-16),25.4 (C-23),23.8 (C-15),22.7 (C-28),20.4 (C-11),19.8 (C-19),19.8 (C-29),19.0 (C-21),18.8 (C-27),18.0 (C-26),11.6 (C-18)。以上数据与文献报道的一致[14],故鉴定化合物 **11** 为 5-烯-7α-羟基谷甾醇。

化合物 12 白色针状结晶。经与 β-谷甾醇的标准品对照,其 R_f 值及显色反应均一致,故确定化合物 **12** 为 β-谷甾醇。

参考文献

1 Xie ZW(谢宗万). Compliation of Countrywide Herbal Medicine of China (全国中草药汇编). Beijing:People's Medical Publishing House,1996.

2 Hu Y(胡跃). Research progress of reseratrol on antitumor adivity. *Foreigen Med Sci Section Ondclogy*(国外医学,肿瘤学分册),2002,29:174-l77.

3 Xiao D(肖东),Gu ZL(顾振纶). Idendification of radix ginseng and Radix *Panacis quinquefolii* by thermogravimetric analysis. *Chin Tradit Pat Med*(中成药),1997,19:31-32.

4 Tie GC(铁桂春),Liu HX(刘红献). Resources and development and utilization prospects of Da Tong's *Rumex patientia* L. *Qinghai Prata*(青海草业),1998,7:32-33.

5 Schleich S, Papaioannou M, Baniahmad A, *et al*. Activity-guided isolation of antiandrogenic compound of *Pygeum africanum*. *Planta Med*,2006,72:547-551.

6 Yu TW,Shen Y,McDaniel R,*et al*. Engineered biosynthesis of novel polyketides from *Streptomyces* spore pigment polyketide synthases. *Am Chem Soc*,1998,120:7749-7759.

7 Fan JP(范积平),Zhang ZL(张贞良). Studies on the chemical constituents of *Rumex crispus*. *Chin Med Mater*(中药材),2009,32:1836-1840.

8 Hasnah M,Sirat,Rezali MF,*et al*. Isolation and identification of radical scavenging and tyrosinase inhibition of polyphenols from *Tibouchina semidecandra* L. *Agric Food Chem*,2010,58:10404-10409.

9 Matsunaga K,Shibuya M,Ohizumi Y. Imperanene,a novel phenolic compound with platelet aggregation inhibitory activity from *Imperata cylindrica*. *J Nat Prod*,1995,58:138-139.

10 Yasuhiro H,ShuJi O,Takashi S. Extractives of chosenia arbutifolia A. Skvortz. II. New neolignans from the wood of *Chosenia arbutifolia*. *Mokuzai Gakkaishi*,1994,40:549-553.

11 Moon SS,Rahman AA,Kim JY,*et al*. Hanultarin,a cytotoxic lignan as an inhibitor of actin cytoskeleton polymerization from the seeds of *Trichosanthes kirilowii*. *Bioorg Med Chem*,2008,16:7264-7269.

12 Achenbach H,Löwel M,Waibel R,*et al*. New lignan glucosides from *Stemmadenia minima*. *Planta Med*,1992,58:270-272.

13 Zhou JS,Zhang TT,Chen JJ,*et al*. Chemical constituents from the roots of *Streptocaulon griffithii*. *Chin J Nat Med*,2009,7:108-110.

14 Zhang Y(张宇),Zhao H(赵宏). The chemical constituents from leaves of acer saccharum. *Chin J Nat Med*(中药材)2009,3:361-362.