青阳参乙酸乙酯萃取部位的化学成分

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摘 要 从青阳参(*Cynanchum otophyllum* Schneid.)醇提取物的乙酸乙酯萃取部位分离出14个化合物,通过波谱方法和理化性质分别鉴定为青阳参苷甲(**1**),青阳参苷乙(**2**),2,5-二羟基苯乙酮(**3**),2,5-二羟基苯甲酸甲酯(**4**),香草醛(**5**),阿江榄仁酸(**6**),山橘脂酸(**7**),告达亭3-*O*-*β*-D-吡喃加拿大麻糖基-(1→4)-*β*-D-吡喃夹竹桃糖基-(1→4)-*β*-D-吡喃加拿大麻糖基-(1→4)-*β*-D-吡喃加拿大麻糖苷(**8**),本波苷元(**9**),告达亭3-*O*-*β*-D-葡萄吡喃糖基-(1→4)-*β*-D-夹竹桃吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖苷(**10**),青阳参苷元3-*O*-*β*-D-夹竹桃吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-洋地黄毒吡喃糖苷(**11**),凯德苷元3-*O*-*β*-D-加拿大麻吡喃糖苷(**12**),青阳参苷元3-*O*-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-洋地黄毒吡喃糖苷(**13**),凯德苷元3-*O*-*β*-D-夹竹桃吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖苷(**14**)。其中化合物**6**和**7**为首次从鹅绒藤属中分离得到,化合物**3**~**5**、**8**~**14**为首次从该植物中分离得到。

关键词 青阳参;甾体苷;化学成分;结构鉴定

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Chemical constituents from ethyl acetate extract of *Cynanchum otophyllum* Schneid.

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Abstract Fourteen compounds were isolated and purified from ethyl acetate extract of *Cynanchum otophyllum* Schneid., and were identified as otophylloside A(**1**), otophylloside B(**2**), 2, 5-dihydroxyacetophenone(**3**), methyl 2, 5-dihydroxy-benzoate(**4**), vanillin(**5**), arjunolic acid(**6**), glycosmisic acid(**7**), caudatin-3-*O*-*β*-D- cymaropyranosyl-(1→4)-*β*-D-oleandropyranosl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside(**8**), penupogenin(**9**), caudatin-3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-oleandropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside(**10**), qingyangshengenin-3-*O*-*β*-D-oleandropyranosyl-(1→4)-*β*-D- cymaropyranosyl-(1→4)-*β*-D-digitoxopyranoside(**11**), and kidjoranin-3-*O*-*β*-D- cymaropyranoside(**12**), qingyangshengenin-3-*O*-*β*-D-cymaropyranosyl-(1→4)-*β*-D- digitoxopyranoside(**13**), and kidjoranin-3-*O*-*β*-D-oleandropyranosyl-(1→4)-*β*-D- cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside(**14**) by physicochemical properties and spectroscopic analyses. Among them, compounds **6-7** were firstly isolated from the genus *Cynanchum*, and compounds **3-5, 8-14** were isolated from this plant for the first time.

Key words *Cynanchum otophyllum*; steroids; chemical constituents; structural identification

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青阳参(*Cynanchum otophyllum* Schneid.)为萝摩科鹅绒藤属(*Cynanchum* Linn.)植物,又名青羊参、青洋参、千年生、奶浆藤等,产于云南、湖南、广西、贵州、四川和西藏等省区,生长于海拔1 500~2 800 m的山地、溪谷疏林中或山坡路边[1]。《彝药志》记载具有益肾强筋、健脾和胃、祛风除湿、解毒、镇静、驱虫的功效;《滇南本草》记载:"民间用作壮腰健肾,强筋壮骨"。青阳参性微温,味甘微苦,具有补气益肾、强筋壮骨、活血散癖、祛痰止咳、除湿解毒的作用。常用于治疗子宫肌瘤、腰肌劳损和跌打损伤等引起的腰痛以及肺结核与子宫内膜结核等疾病[2]。现已开发出的青阳参片是云南特有中成药,其有效成分为青阳参总苷。为进一步研究其有效成分,本文采用现代色谱分离方法和光谱鉴定技术,对青阳参进行了研究,从乙酸乙酯部位分离并鉴定了14个化合物,其中化合物**6**和**7**为首次从鹅绒藤属中分离得到,化合物**3**~**5**、**8**~**14**为首次从该植物中分离得到。

1 仪器与材料

X-4熔点测定仪(温度计未校正);Bruker AV-500和AV-300型核磁共振仪;Agilent 1100 Series LC/MSD Trap质谱仪。柱色谱硅胶(青岛海洋化工厂)和薄层色谱硅胶GF_{254}(烟台化工研究所);Sephadex LH-20(美国Pharmacia公司);MCI HP-20(日本三菱化学公司);ODS(德国默克公司);所用试剂均为市售分析纯。

青阳参药材购于2010年3月,产地云南,经中国药科大学秦民坚教授鉴定为青阳参(*Cynanchum otophyllum* Schneid.)的根,标本(No. 20100306)保存于中国药科大学天然药物化学教研室。

2 提取与分离

干燥的青阳参根茎19.5 kg,分别用80%,70%,70%乙醇加热回流提取3次,每次2 h,提取液减压浓缩至无醇味,加水混悬后依次用石油醚、乙酸乙酯及正丁醇萃取。乙酸乙酯萃取部位(580 g)经硅胶柱色谱,以二氯甲烷-甲醇梯度洗脱(100∶0→100∶9),TLC检识,合并得到9个流分(Fr. 1~9)。Fr. 1经硅胶柱色谱石油醚-乙酸乙酯梯度洗脱(10∶1→4∶1),制备TLC,得化合物**3**(20 mg)、**4**(20 mg)。Fr. 2经硅胶柱色谱石油醚-乙酸乙酯梯度洗脱(10∶1→2∶1),反复Sephadex LH-20柱色谱以甲醇洗脱纯化,得化合物**2**(100 mg)、**5**(20 mg)、**8**(30 mg)。Fr. 3经硅胶柱色谱以二氯甲烷-甲醇(20∶1→1∶1)梯度洗脱,反复ODS柱色谱以乙腈-水梯度洗脱纯化,得化合物**6**(10 mg)、**7**(20 mg)、**9**(10 mg)、**10**(60 mg)、**11**(100 mg)。Fr. 4经MCI柱色谱以甲醇-水(50∶50→100∶0)梯度洗脱,反复ODS柱色谱以乙腈-水梯度洗脱纯化,得化合物**1**(10 mg)、**12**(20 mg)、**13**(20 mg)、**14**(20 mg)。上述化合物结构式见图1。

3 结构鉴定

化合物**3** 黄绿色针晶,mp 174~176 ℃。^{1}H NMR (DMSO-d_6,300 MHz) δ:11.32(1H,s,2-OH),9.18(1H,s,5-OH),7.18(1H,d,J = 2.9 Hz,H-6),7.00(1H,dd,J = 2.9,8.8 Hz,H-4),6.83(1H,d,J = 8.8 Hz,H-3),2.58(3H,s,H-8)。^{13}C NMR (DMSO-d_6,75 MHz) δ:203.9(C-7),153.7(C-2),149.3(C-5),124.4(C-4),120.1(C-6),118.2(C-3),115.3(C-1),27.6(C-8)。以上波谱数据与文献[3]报道一致,故鉴定化合物**3**为2,5-二羟基苯乙酮(2,5-dihydroxyacetophenone)。

化合物**4** 白色粉末(石油醚-丙酮),mp 107~109 ℃。^{1}H NMR (DMSO-d_6,300 MHz) δ:12.43(1H,br. s,2-OH),9.82(1H,s,5-OH),7.45(1H,d,J = 1.9 Hz,H-6),7.43(1H,d,J = 8.8 Hz,H-3),6.83(1H,dd,J = 2.2,8.8 Hz,H-4),3.78(3H,s,H-8)。^{13}C NMR (DMSO-d_6,75 MHz) δ:167.2(C-7),151.1(C-2),147.2(C-5),123.4(C-4),121.6(C-1),115.1(C-3),112.7(C-6),55.5(C-8)。以上波谱数据与文献[4]报道一致,故鉴定化合物**4**为2,5-二羟基苯甲酸甲酯(methyl 2,5-dihydroxybenzoate)。

化合物**5** 无色针状晶体(石油醚),mp 79~81 ℃。ESI-MS m/z:151[M-H]$^-$、136[M-H-CH_3]$^-$。与香草醛对照品在HPTLC中的R_f及显色行为一致,且两者混合熔点不下降,故鉴定化合物**5**为香草醛(vanillin)。

化合物**6** 白色无定形粉末(甲醇),mp 312~314 ℃。^{1}H NMR (C_5D_5N,500 MHz) δ:5.44(1H,br. s,H-12),4.22(1H,d,br,H-2),4.20(1H,d,J = 4.2 Hz,H-3),4.18(1H,m,H-23α),3.70(1H,d,J = 10.4 Hz,H-23β),3.26(1H,dd,J = 13.4,4.2 Hz,H-18),1.18、1.05、1.04、1.02、0.97、0.89

(each 3H, s, Me-24、25、26、27、29、30)。^{13}C NMR (C_5D_5N, 125 MHz) δ: 180.2 (C-28), 144.9 (C-13), 122.5 (C-12), 78.4 (C-3), 68.9 (C-2), 66.7 (C-23), 48.2 (C-9), 48.1 (C-5), 47.7 (C-17), 46.7 (C-1), 46.4 (C-19), 43.6 (C-4), 42.3 (C-14), 42.0 (C-18), 39.9 (C-8), 38.5 (C-10), 34.2 (C-21), 33.2 (C-7), 32.9 (C-22), 30.9 (C-20), 30.0 (C-29), 28.3 (C-15), 26.2 (C-27), 24.0 (C-11), 23.8 (C-16), 23.7 (C-30), 18.6 (C-6), 17.5 (C-25), 17.1 (C-26), 14.2 (C-24)。以上波谱数据与文献[5]报道一致,故鉴定化合物 **6** 为阿江榄仁酸(arjunolic acid)。

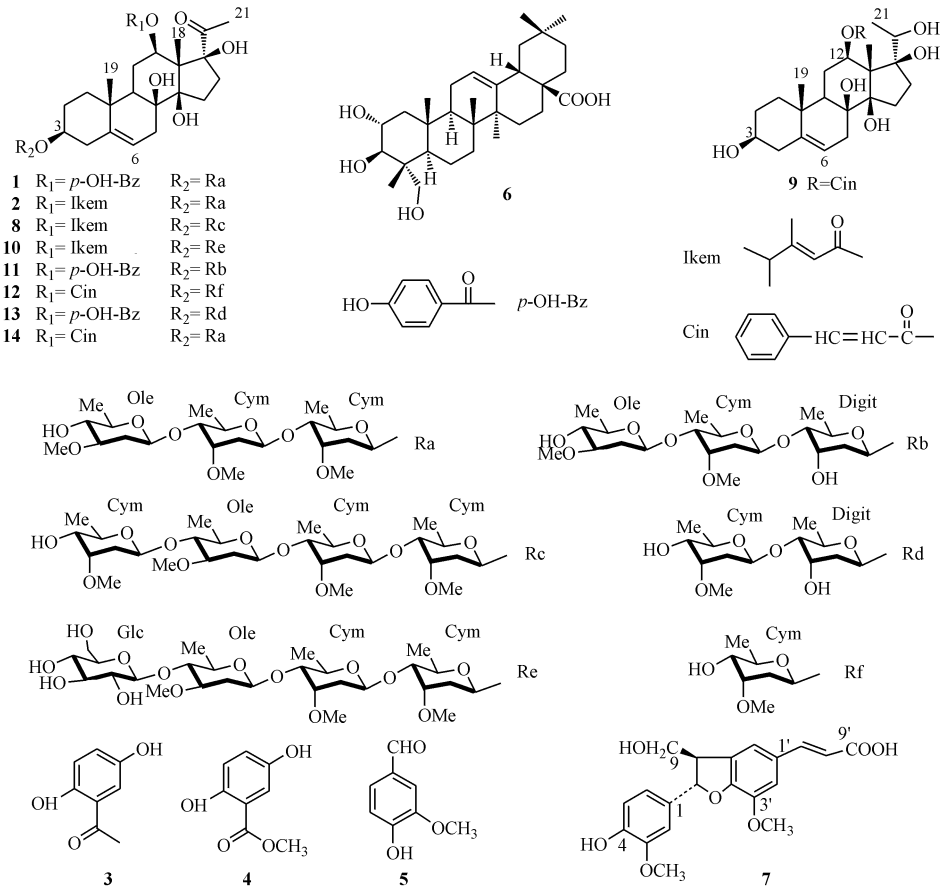

Figure 1　Chemical structures of compounds **1-14**

Digit: digitoxopyranosyl; Cym: cymaropyranosyl; Ole: oleandropyranosyl; Glc: Glucopyranosyl

化合物 **7**　白色粉末(甲醇), mp 239 ~ 240 ℃。^{1}H NMR (DMSO-d_6, 300 MHz) δ: 12.17 (1H, s, COOH), 9.03 (1H, s, 4-OH), 7.52 (1H, d, J = 15.9 Hz, H-7′), 7.24 (2H, br. s, H-2′, 6′), 6.92 (1H, br. s, H-2), 6.76 (2H, br. s, H-5, 6), 6.38 (1H, d, J = 15.9 Hz, H-8′), 5.53 (1H, d, J = 6.6 Hz, H-7), 5.04 (1H, br. s, 9-OH), 3.83 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.69 (1H, m, H-9α), 3.49 (1H, dd, J = 6.1, 12.2 Hz, H-9β)。^{13}C NMR (DMSO-d_6, 75 MHz) δ: 167.9 (C-9′), 149.7 (C-4′), 147.6 (C-3), 146.5 (C-4), 144.5 (C-7′), 143.9 (C-3′), 131.9 (C-5′), 129.8 (C-1), 127.8 (C-1′), 118.6 (C-6), 117.8 (C-6′), 116.1 (C-8′), 115.3 (C-5), 112.3 (C-2′), 110.4 (C-2), 87.9 (C-7), 62.7 (C-9), 55.8 (OCH_3), 55.6 (OCH_3), 56.6 (C-8)。以上波谱数据与文献[6]报道一致,故鉴定化合物 **7** 为山橘脂酸(glycosmisic acid)。

化合物 **8**　白色粉末(甲醇), mp 150 ~ 151 ℃。^{1}H NMR (C_5D_5N, 500 MHz) δ: 5.87 (1H, t, J = 1.0 Hz, H-2′), 5.30 (1H, m, H-6), 5.28 (1H, dd, J = 9.5, 2.0 Hz, H-1″), 5.26 (1H, dd, J = 9.7, 1.9 Hz, H-1‴′), 5.12 (1H, dd, J = 9.6, 1.7 Hz, H-1‴), 5.04 (1H, dd, J = 11.6, 4.2 Hz, H-12), 4.70 (1H, dd, J = 9.7, 1.9 Hz, H-1⁗), 3.85 (1H, m, H-3), 3.63 (3H, s, OMe″), 3.58 (3H, s, OMe‴), 3.53 (3H, s, OMe⁗), 3.47 (3H, s, OMe‴′), 2.53 (3H, s, H-21), 2.28 (3H, d, J = 1.2 Hz, H-7′), 1.98 (3H, s, H-18), 1.58 (3H, d, J = 6.2 Hz, H-6‴′), 1.46 (3H, d, J = 5.8 Hz, H-6⁗), 1.40 (3H, d, J = 6.2 Hz, H-6″), 1.38 (3H, d, J = 6.2 Hz, H-6‴), 1.33 (3H, s, H-19), 0.96 (6H, t, J = 7.2 Hz, H-6′), 0.97 (6H, t, J = 7.2 Hz, H-5′)。^{13}C NMR (C_5D_5N, 125 MHz) 数

据见表1和表2。以上波谱数据与文献[7]报道一致,故鉴定化合物**8**为告达亭3-*O*-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-夹竹桃吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖苷[caudatin-3-*O*-*β*-D-cymaropyranosyl-(1→4)-*β*-D-oleandropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside]。

化合物**9** 白色粉末(甲醇),mp 145 ~ 150 ℃。^{1}H NMR(C_5D_5N,500 MHz) δ:8.14(1H,d,J = 16.0 Hz,H-3′),7.50(2H,m,H-5′,9′),7.26(3H,m,H-6′,7′,8′),6.95(1H,d,J = 16.0 Hz,H-2′),5.39(1H,br. s,H-6),5.28(1H,dd,J = 11.5,4.1 Hz,H-12),4.10(1H,dd,J = 12.2,6.0 Hz,H-20),3.87(1H,m,H-3),2.15(3H,s,H-19),1.41(3H,s,H-18),1.32(3H,d,J = 6.1 Hz,H-21)。^{13}C NMR(C_5D_5N,125 MHz)数据见表1。以上波谱数据与文献[8]报道一致,故鉴定化合物**9**为本波苷元(penupogenin)。

化合物**10** 白色粉末(甲醇),mp 170 ~ 171 ℃。^{1}H NMR(C_5D_5N,500 MHz) δ:5.84(1H,br. s,H-2′),5.26(1H,br. s,H-6),5.25(1H,br. s,H-1″),5.09(1H,d,J = 7.9 Hz,H-1‴),5.08(1H,d,J = 7.9 Hz,H-1⁗),5.01(1H,dd,J = 11.7,4.1 Hz,H-12),4.66(1H,br. d,J = 9.5 Hz,H-1⁗),4.49(1H,dd,J = 11.5,2.6 Hz,H-6α⁗),4.31(1H,dd,J = 11.5,5.6 Hz,H-6β⁗),3.82(1H,m,H-3),3.59(3H,s,OMe‴),3.55(3H,s,OMe⁗),3.51(3H,s,OMe⁗),2.50(3H,s,H-21),2.26(3H,br. s,H-7′),1.96(3H,s,H-18),1.68(3H,d,J = 6.0 Hz,H-6⁗),1.39(3H,d,J = 6.1 Hz,H-6″),1.37(3H,d,J = 6.2 Hz,H-6‴),1.31(3H,s,H-19),0.95(3H,t,J = 7.2 Hz,H-5′),0.92(3H,t,J = 7.1 Hz,H-6′)。^{13}C NMR(C_5D_5N,125 MHz)数据见表1和表2。以上波谱数据与文献[9]报道一致,故确定化合物**10**为告达亭3-*O*-*β*-D-葡萄吡喃糖基-(1→4)-*β*-D-夹竹桃吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖基-(1→4)-*β*-D-加拿大麻吡喃糖苷[caudatin-3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-oleandropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside]。

Table 1 ^{13}C NMR data for the aglycone of compounds **8-14**

Carbon	Compd. **8**	Compd. **9**	Compd. **10**	Compd. **11**	Compd. **12**	Compd. **13**	Compd. **14**
1	38.99	39.15	39.29	39.55	38.95	39.24	39.29
2	29.87	32.01	29.86	30.36	29.88	29.96	29.88
3	77.69	71.57	77.68	78.27	77.54	77.65	77.67
4	39.30	43.32	38.98	39.43	39.28	39.07	38.96
5	139.43	140.03	139.42	139.92	139.43	139.41	139.41
6	119.14	118.87	119.14	119.62	119.13	119.10	119.23
7	34.82	35.05	33.83	35.30	33.85	34.78	34.80
8	74.32	74.83	74.31	74.85	74.32	74.33	74.33
9	44.62	44.18	44.61	44.99	44.54	44.47	44.55
10	37.43	37.25	37.42	37.91	37.44	37.40	37.45
11	25.07	25.74	25.07	25.65	25.02	25.13	25.06
12	72.61	70.97	72.61	73.88	73.63	73.36	73.65
13	55.00	56.96	57.99	59.34	58.11	58.40	58.14
14	89.45	88.63	89.45	90.05	89.47	89.54	89.50
15	33.83	34.24	34.81	34.38	34.80	33.85	33.85
16	32.96	32.95	32.95	33.68	33.04	33.17	33.08
17	92.40	88.84	92.40	93.00	92.42	92.48	92.44
18	10.60	11.71	10.68	11.32	10.66	10.81	10.70
19	18.18	18.32	18.17	18.66	18.19	18.14	18.20
20	209.33	74.26	209.34	210.30	209.75	210.00	209.86
21	27.50	19.32	27.50	28.27	27.66	27.75	27.70
1′	165.96	167.00	165.96	165.87	165.81	165.35	165.83
2′	114.20	119.64	114.19	122.53	119.20	122.02	119.18
3′	165.35	145.25	165.35	132.91	144.93	132.39	144.95
4′	38.16	135.00	38.15	116.69	135.82	116.17	135.05
5′	20.95	128.58	20.94	164.09	128.57	163.57	129.33
6′	20.86	129.15	20.85	116.69	129.30	116.17	128.60
7′	16.47	130.49	16.46	132.91	130.58	132.39	130.61
8′		129.15			129.30		128.60
9′		128.58			128.57		129.33

Table 2　^{13}C NMR data for the sugar moieties of compounds **8**,**10-14**

Position	Compd. **8**	Compd. **10**	Compd. **11**	Compd. **12**	Compd. **13**	Compd. **14**
	D-Cym	D-Cym	D-Digit	D-Cym	D-Digit	D-Cym
1″	96.43	96.42	96.88	96.33	96.37	96.42
2″	37.25	37.25	39.76	36.12	38.91	37.26
3″	78.04	78.11	68.04	78.92	67.48	77.85
4″	83.42	83.28	83.89	74.25	83.45	83.43
5″	69.06	68.91	69.10	70.95	68.62	69.00
6″	18.50	18.49	19.17	19.09	18.66	18.56
OMe	58.85	58.89		58.03		58.89
	D-Cym′	D-Cym′	D-Cym		D-Cym	D-Cym′
1‴′	100.46	100.45	100.27		99.73	100.49
2‴′	37.06	37.05	37.72		35.64	37.26
3‴′	77.80	77.78	78.19		78.78	78.06
4‴′	83.19	83.23	83.62		74.06	83.16
5‴′	68.93	69.05	69.63		70.99	69.08
6‴′	18.60	18.60	19.01		18.87	18.62
OMe	58.94	59.00	58.91		58.07	58.89
	D-Ole	D-Ole	D-Ole			D-Ole
1⁗	101.97	101.88	102.66			102.17
2⁗	37.69	37.46	37.20			36.99
3⁗	77.88	79.33	81.87			81.43
4⁗	82.71	83.14	76.71			76.24
5⁗	71.81	72.04	73.45			72.98
6⁗	18.70	18.85	19.01			18.68
OMe	57.32	57.21	57.55			57.06
	D-Cym″	D-Glc				
1⁗′	98.50	104.48				
2⁗′	35.88	75.72				
3⁗′	79.00	78.70				
4⁗′	74.21	72.08				
5⁗′	71.24	78.04				
6⁗′	19.02	63.16				
OMe	57.99					

化合物 **11**　白色粉末(甲醇),mp 197 ~ 199 ℃。^{1}H NMR(C_5D_5N,500 MHz) δ:8.32(2H,d,J = 8.8 Hz,H-3′,7′),7.26(2H,d,J = 8.8 Hz,H-4′,6′),6.20(1H,br. s,H-6),5.50(1H,dd,J = 9.5,1.7 Hz,H-1″),5.35(1H,dd,J = 11.7,4.2 Hz,H-12),5.20(1H,dd,J = 9.6,1.8 Hz,H-1‴),4.78(1H,dd,J = 9.7,1.8 Hz,H-1⁗),3.88(1H,m,H-3),3.60(3H,s,OMe″′),3.50(3H,s,OMe⁗),2.44(3H,s,H-21),2.11(3H,s,H-18),1.59(3H,d,J = 6.1 Hz,H-6⁗),1.47(3H,d,J = 6.3,H-6‴),1.39(3H,d,J = 6.3 Hz,H-6″),1.34(3H,s,H-19)。^{13}C NMR(C_5D_5N,125 MHz)数据见表 1 和表 2。以上波谱数据与文献[10]报道一致,可确定化合物 **11** 为青阳参苷元 3-*O*-β-D-夹竹桃吡喃糖基-(1→4)-β-D-加拿大麻吡喃糖基-(1→4)-β-D-洋地黄毒吡喃糖苷[qingyangshengenin-3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranoside]。

化合物 **12**　白色粉末(甲醇),mp 166 ~ 169 ℃。^{1}H NMR(C_5D_5N,500 MHz) δ:7.97(1H,d,J = 16.0 Hz,H-3′),7.60(2H,m,H-5′,9′),7.32(3H,m,H-6′,7′,8′),6.79(1H,d,J = 16.0 Hz,H-2′),5.30(1H,br. d,J = 4.8 Hz,H-6),5.22(1H,dd,J = 9.5,1.9 Hz,H-1″),5.16(1H,dd,J = 11.6,4.2 Hz,H-12),3.86(1H,m,H-3),2.47(3H,s,H-21),2.07(3H,s,H-18),1.54(3H,d,J = 6.2 Hz,H-6″),1.34(3H,s,H-19)。^{13}C NMR(C_5D_5N,125 MHz)数据见表 1 和表 2。以上波谱数据与文献[11]报道一致,故鉴定化合物 **12** 为凯德苷元 3-*O*-β-D-加拿大麻吡喃糖苷[kidjoranin-3-*O*-β-D- cymaropyranoside]。

化合物 **13**　白色粉末(甲醇),mp 164 ~ 165 ℃。^{1}H NMR(C_5D_5N,500 MHz) δ:8.27(2H,d,J = 8.7 Hz,H-3′,7′),7.20(2H,d,J = 8.8 Hz,H-4′,6′),5.46(1H,dd,J = 9.5,1.6 Hz,H-1″),5.30(1H,dd,J = 11.6,4.2 Hz,H-12),5.26(1H,br. d,J = 4.3 Hz,H-6),5.10(1H,dd,J = 9.7,1.7 Hz,H-1‴),3.85(1H,m,H-3),3.44(3H,s,OMe″′),2.39(3H,s,H-21),2.06(3H,s,H-18),1.43(3H,d,J = 6.2,H-6⁗),1.42(3H,d,J = 6.2 Hz,H-6″),1.28(3H,s,H-19)。^{13}C NMR(C_5D_5N,125 MHz)数据见表 1 和表 2。以上波谱数据与文献[10]报道一致,故确定化合物 **13** 为青阳参苷元 3-*O*-β-D-加拿大麻吡喃糖基-(1→4)-β-D-洋地黄毒吡喃糖苷[qingyangshengenin-3-*O*-β-D- cymaropyranosyl-(1→4)-

β-D-digitoxopyranoside]。

化合物 **14** 白色粉末(甲醇),mp 158 ~ 159 ℃。^{1}H NMR(C_5D_5N,300 MHz) δ:7.97(1H,d,*J* = 16.0 Hz,H-3′),7.61(2H,m,H-5′,9′),7.32(3H,m,H-6′,7′,8′),6.79(1H,d,*J* = 16.0 Hz,H-2′),5.29(1H,br. s,H-6),5.28(1H,br. d,*J* = 9.5 Hz,H-1″),5.25(1H,br. d,*J* = 9.5 Hz,H-1‴),4.75(1H,br. d,*J* = 9.4 Hz,H-1⁗),3.84(1H,m,H-3),3.61(3H,s,OMe″),3.56(3H,s,OMe‴),3.44(3H,s,OMe⁗),2.48(3H,s,H-21),2.02(3H,s,H-18),1.55(3H,d,*J* = 6.2 Hz,H-6⁗),1.40(3H,d,*J* = 6.2,H-6‴),1.38(3H,d,*J* = 6.2 Hz,H-6″),1.33(3H,s,H-19)。^{13}C NMR(C_5D_5N,75 MHz)数据见表1和表2。以上波谱数据与文献[10]报道一致,故鉴定化合物 **14** 为凯德苷元 3-*O*-β-D-夹竹桃吡喃糖基-(1→4)-β-D-加拿大麻吡喃糖基-(1→4)-β-D-加拿大麻吡喃糖苷[kidjoranin-3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside]。

参考文献

[1] Jiang Y, Li BT. *Flora of China*(中国植物志)[M]. Beijing: Science Press, 1977: 377.

[2] Sun YN, Yan JL. Clinical application of *Cynanehum otophyllum* Schneid. as an national medicine[J]. *Chin J Ethnomed Ethnopharm*(中国民族民间医药杂志), 1999, (5): 309.

[3] Lin AQ. *Studies on the Chemical Constituents of Cynanchum Bungei Decne.*(泰山白首乌化学成分的提取、分离与鉴定)[D]. Shangdong: Shandong Traditional Chinese Medicine University, 2005.

[4] Xiang Y, Wang H, Wen YY. Studies on the chemical constituents of *Platycerium wallichii* Hook.[J]. *J Trop Subtrop Bot*(热带亚热带植物学报), 2002, **10**(1): 69 - 73.

[5] Gui MY, Jin YR, Wang BZ. Chemical constituents of *Rabdosia japonica*[J]. *Chin Pharm J*(中国药学杂志), 1999, **34**(8): 516 - 518.

[6] Shen XL, Zeng HF, Chen J, *et al*. Study on chemical constituents isolated from *Glycosmis citrifolia*[J]. *Chin Pharm J*(中国药学杂志), 2002, **37**(1): 14 - 17.

[7] Tsutomu W, Tadataka N. Steroidal glycosides from root of *Cynanchum caudatum* MⅡ[J]. *Chem Pharm Bull*, 1995, **43**(10): 1 734 - 1 737.

[8] Qiu SQ, Zhang ZX, Zhou J. Studies on the constituents from *Marsdenia Globifera*[J]. *Acta Bot Sin*(植物学报), 1990, **32**(12): 936 - 942.

[9] Tsutomu W, Tadataka N. Steroidal glycosides from roots of *Cynanchum caudatum*[J]. *Phytochem*, 1997, **44**(5): 917 - 923.

[10] Chen G, Xu N, Pei YH. C_{21} steroidal glycosides from *Cynanchum wallichii* Wight[J]. *J Asian Nat Prod Res*, 2009, **11**(2): 177 - 182.

[11] Yin M, Feng X, Chen Y, *et al*. A new steroidal glycoside from roots of *Cynanchum auriculatum*[J]. *Chin Herb Med*, 2010, **2**(1): 62 - 64.

·新药信息·

2013年1~5月FDA批准新分子实体药物

序号	商品名	通用名	适应证	批准日期
1	Nesina	alogliptin	2型糖尿病	2013-01-25
2	Kynamro	mipomersen sodium	纯合子型家族性高胆固醇血症	2013-01-29
3	Pomalyst	pomalidomide	多发性骨髓瘤	2013-02-08
4	Kadcyla	ado-trastuzumab emtansine	HER2阳性乳腺癌	2013-02-22
5	Osphena	ospemifene	性交困难	2013-02-26
6	Lymphoseek	technetium Tc 99m tilmanocept	放射性诊断显影剂	2013-03-13
7	Dotarem	gadoterate meglumine	磁共振成像诊断试剂	2013-03-20
8	Tecfidera	dimethyl fumarate	多发性硬化症	2013-03-27
9	Invokana	canagliflozin	2型糖尿病	2013-03-29
10	Breo Ellipta	fluticasone furoate and vilanterol inhalation powder	慢性阻塞性肺病	2013-05-10
11	Xofigo	radium Ra 223 dichloride	晚期前列腺癌	2013-05-15
12	Tafinlar	dabrafenib	黑色素瘤	2013-05-29
13	Mekinist	trametinib	黑色素瘤	2013-05-29

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