文章编号:1001-6880(2012)01-0008-04

云南透骨草的化学成分研究

扶教龙[1],谭昌恒[2*],谭俊杰[2],陈佳佳[1],邱业先[1],朱大元[2]

[1]苏州科技学院化学与生物工程学院,苏州 215009;[2] 中国科学院上海药物研究所新药研究国家重点实验室,上海 201203

摘　要:从云南透骨草全草95%乙醇提取物中分离得到11个化合物,经波谱分析鉴定为山柰酚3-*O*-α-*L*-吡喃鼠李糖苷(**1**),番石榴苷(**2**),滇白珠甲苷(**3**),槲皮苷(**4**),(-)-5′-甲氧基异落叶松脂醇9-*O*-β-D-木糖苷(5),五味子苷(**6**),(－)-表儿茶素(**7**),异槲皮苷(**8**),金鸡纳素Ia(**9**),熊果酸(**10**)和2,5-双-(β-苯乙基)苯酚(**11**)。其中化合物**1**、**2**、**9**和**11**为首次从该植物中分得,化合物**11**是首次报导的天然产物。

关键词:云南透骨草;杜鹃花科;化学成分

中图分类号:R284.1;Q946.91　　**文献标识码**:A

Chemical Constituents of *Gaultheria yunnanensis*

FU Jiao-long[1],TAN Chang-heng[2*],TAN Jun-jie[2],CHEN Jia-jia[1],QIU Ye-xian[1],ZHU Da-yuan[2]

[1]*School of Chemistry and Bioengineering,University of Science and Technology of Suzhou,Suzhou 215009,China*;

[2]*State Key Laboratory of Drug Research,Shanghai Institute of Materia Medica,Chinese Academy of Sciences,Shanghai 201203,China*

Abstract:Eleven compounds were isolated from the 95% ethanol extract of the whole plants of *Gaultheria yunnanensis*, which were identified to be kaempferol 3-*O*-α-*L*-rhamnopyranoside (**1**), guaijaverin (**2**), gaultheroside A (**3**), quercitrin (**4**), (-)-5′-methoxyisolariciresinol 9-*O*-β-D-xylopyranoside (**5**), schizandriside (**6**), (-)-epicatechin (**7**), isoquercitrin (**8**), cinchonain Ia (**9**), ursolic acid (**10**), and 2,5-bis(β-phenylethyl)phenol (**11**). Among them, **1**, **2**, **9** and **11** were firstly obtained from the plant, and **2** was reported as natural compound at the first time.

Key words:*Gaultheria yunnanensis*;Ericaceae;chemical constituents

云南透骨草(*Gaultheria yunnanensis*),又名滇白珠、透骨香、九木香等,为杜鹃花科白珠属植物,具有清热解毒、活血化瘀、祛风除湿、顺气平喘的功能,主治风湿病、眩晕、闭经、风寒感冒、咳嗽、哮喘等症[1]。我们对采自云南的云南透骨草全草进行了化学成分研究,从中分离并鉴定了11个化合物,分别为山柰酚3-*O*-α-*L*-吡喃鼠李糖苷(**1**),番石榴苷(**2**),滇白珠甲苷(**3**),槲皮苷(**4**),(－)-5′-甲氧基异落叶松脂醇9-*O*-β-D-木糖苷(**5**),五味子苷(**6**),(－)-表儿茶素(**7**),异槲皮苷(**8**),金鸡纳素Ia(**9**),熊果酸(**10**)和2,5-双-(β-苯乙基)苯酚(**11**)。其中,化合物**1**、**2**、**9**和**11**为首次从该植物中分得,化合物**11**是首次报导的天然产物。

1　实验部分

1.1　仪器与材料

Finnigan-MAT-95质谱仪;Bruker DRX 400核磁共振仪,TMS为内标;Nicolet Magna 750 FTIR型红外分光光度仪;柱层析用硅胶(青岛海洋化工厂);薄层层析硅胶预制板$HSGF_{254}$(烟台化工研究院);葡聚糖凝胶Sephadex LH-20(Pharmacia Biotech AB,Uppsala,Sweden);反相硅胶LiChrospher 100 Rp-18(50 μm)(Merck);其他各种溶剂均为分析纯。云南透骨草全草于2005年5月采集于云南,由中国科学院上海药物研究所黄骥博士鉴定。

1.2　提取与分离

干燥的云南透骨草全草10 kg用95%乙醇提取三次(15 L × 3),浓缩成浸膏(1.5 kg),将浸膏悬浮于4 L水中,然后分别用等量石油醚、乙酸乙酯和正丁醇各萃取三次,减压浓缩,得石油醚部位(35 g)、乙酸乙酯部位(195 g)和正丁醇部位(890 g)。经大孔树脂、硅胶、Sephadex LH-20和反相硅胶柱层析分离纯化,从乙酸乙酯部位分得**1**(13 mg)、**2**(16 mg)、**3**(27 mg)、**4**(27 mg)、**5**(24 mg)、**6**(32 mg)、**7**(41 mg)、**8**(31 mg)和**9**(27 mg);从正丁醇部位分得**10**(19 mg)和**11**(62 mg)。

收稿日期:2010-07-02　　接受日期:2010-08-31

*通讯作者 Tel:86-21-50806600;E-mail:chtan@mail.shcnc.ac.cn

2 结构鉴定

化合物 1 $C_{21}H_{20}O_{10}$,黄色粉末。$[\alpha]_D^{20}$-152°(*c* 0.12,MeOH);ESI-MS *m/z*:455([M + Na]$^+$),887[2M + Na]$^+$,431[M - H]$^-$)和 863[2M - H]$^-$;^{1}H NMR(400 MHz,CD_3OD)δ:7.78(2H,d,*J* =8.8 Hz,H-2′,H-6′),6.94(2H,d,*J* =8.8 Hz,H-3′,H-5′),6.33(1H,d,*J* =2.1 Hz,H-8),6.18(1H,d,*J* =2.1 Hz,H-6),5.52(1H,dd,*J* =1.6,3.4 Hz,H-2″),5.47(1H,d,*J* =1.6 Hz,H-1″),3.93(1H,dd,*J* =3.4,9.0 Hz,H-3″),3.39(1H,t,*J* =9.0 Hz,H-4″),3.39(1H,m,H-5″),0.98(3H,d,*J* =5.8 Hz,H-6″);^{13}C NMR(100 MHz,CD_3OD)δ:179.4(C-4),166.3(C-7),163.2(C-5),161.7(C-4′),159.2(C-2),158.6(C-9),135.6(C-3),131.8(2C,C-2′ and C-6′),122.5(C-1′),116.7(2C,C-3′ and C-5′),105.8(C-10),100.5(C-1″),100.0(C-6),94.9(C-8),73.6(C-4″),73.4(C-2″),72.1(C-5″),70.7(C-3″),18.2(C-6″)。以上数据与文献[2]报道的山奈酚 3-*O*-α-*L*-吡喃鼠李糖苷(Kaempferol 3-*O*-α-*L*-rhamnopyranoside)一致。

化合物 2 $C_{20}H_{18}O_{11}$,黄色粉末。$[\alpha]_D^{20}$-35°(*c* 0.15,MeOH);ESI-MS *m/z*:457[M + Na]$^+$,891[2M + Na]$^+$和 433[M - H]$^-$;^{1}H NMR(400 MHz,CD_3OD)δ:7.75(2H,d,*J* =8.7 Hz,H-2′ and H-6′),6.96(2H,d,*J* =8.6 Hz,H-3′ and H-5′),6.35(1H,d,*J* =2.1 Hz,H-8),6.18(1H,d,*J* =2.1 Hz,H-6),5.43(1H,d,*J* =1.6 Hz,H-1″);^{13}C NMR(100 MHz,CD_3OD)δ:180.0(C-4),166.5(C-7),163.5(C-5),159.2(C-9),158.9(C-2),150.5(C-4′),146.5(C-3′),136.1(C-3),123.5(C-6′),123.4(C-1′),117.9(C-5′),116.7(C-2′),106.2(C-10),105.1(C-1″),100.4(C-6),95.2(C-8),74.6(C-2″),73.4(C-3″),69.6(C-4″),67.5(C-5″)。以上数据与文献[3,4]报道的番石榴苷(Guaijaverin)一致。

化合物 3 $C_{27}H_{36}O_{12}$,白色粉末。$[\alpha]_D^{20}$ +24°(*c* 0.20,MeOH);ESI-MS *m/z*:575[M + Na]$^+$,1127[2M + Na]$^+$和 551[M - H]$^-$;^{1}H NMR(400 MHz,CD_3OD)δ:6.55(1H,s,H-5),6.42(2H,s,H-2′ and H-6′),5.08(1H,m,H-1),4.80(1H,d,*J* =7.6 Hz,H-1″),4.38(1H,m,H-2a),4.28(1H,m,H-5″),4.27 Hz,H-4a),4.15(1H,m,H-4″),4.11(1H,m,H-3″),4.08(2H,m,H-3a),4.02(1H,m,H-2″),3.90(1H,dd,*J* =9.77,3.97 Hz,H-2a),3.78(6H,s,OMe-3′,-5′),3.76(3H,s,OMe-6),3.73(3H,s,OMe-8),3.64(1H,m,H-5″),3.13(1H,dd,*J* =14.95,11.90 Hz,H-4b),3.04(1H,dd,*J* =14.95,4.28 Hz,H-4),2.69(1H,m,H-2),2.17(1H,m,H-3);^{13}C NMR(100 MHz,CD_3OD)δ:149.4(2C,C-3′ and C-5′),149.1(C-8),148.1(C-6),139.9(C-7),139.4(C-1′),134.9(C-4′),130.6(C-10),126.9(C-9),108.2(C-5),107.4(2C,C-2′ and C-6′),106.0(C-1″),78.5(C-3″),75.4(C-2″),71.7(C-4″),71.4(C-2a),67.5(C-5″),66.5(C-3a),60.5(OMe-8),57.3(2C,OMe-3′ and OMe-5′),57.0(OMe-6),47.2(C-2),43.5(C-1),41.0(C-3),34.4(C-4)。以上数据与文献[5,6]报道的滇白珠甲苷(Gaultheroside A)一致。

化合物 4 $C_{21}H_{20}O_{11}$,黄色粉末。$[\alpha]_D^{20}$ -145°(*c* 0.18,MeOH);ESI-MS *m/z*:471[M + Na]$^+$,919[2M + Na]$^+$,447[M - H]$^-$和 895[2M - H]$^-$;^{1}H NMR(400 MHz,CD_3OD)δ:7.30(1H,d,*J* =2.5 Hz,H-2′),7.26(1H,dd,*J* =2.1,9.0 Hz,H-6′),6.88(1H,d,*J* =8.0 Hz,H-5′),6.41(1H,d,*J* =2.0 Hz,H-8),6.22(1H,d,*J* =2.0 Hz,H-6),5.26(1H,d,*J* =0.8 Hz,H-1″),0.95(3H,d,*J* =5.9 Hz,H-6″);^{13}C NMR(100 MHz,CD_3OD)δ:179.8(C-4),165.9(C-7),163.3(C-5),159.5(C-9),158.7(C-2),150.0(C-4′),146.5(C-3′),136.6(C-3),123.4(2C,C-1′ and C-6′),117.4(C-5′),116.7(C-2′),106.2(C-10),103.8(C-1″),100.2(C-6),95.2(C-8),73.7(C-4″),72.5(C-3″),72.3(2C,C-2″ and C-5″),18.0(C-6″)。以上数据与文献[7]报道的槲皮苷(Quercitrin)一致。

化合物 5 $C_{26}H_{34}O_{11}$,白色粉末。$[\alpha]_D^{20}$ -31°(*c* 0.21,MeOH);ESI-MS *m/z*:545[M + Na]$^+$,1067[2M + Na]$^+$和 521[M - H]$^-$;^{1}H NMR(400 MHz,CD_3OD)δ:6.98(2H,s,H-2′ and H-6′),6.88(2H,s,H-5 and H-8),4.60(1H,d,*J* =7.3 Hz,H-1″),4.56(1H,d,*J* =10.4 Hz,H-2a),4.51(1H,d,*J* =10.9 Hz,H-1),4.26(1H,t,*J* =5.8,5.5 Hz,H-5″),4.16(1H,m,H-4″),4.05(1H,m,H-3″),3.99(1H,m,H-2″),3.78(6H,s,OMe-3′ and OMe-5′),4.22(2H,m,H-3a),3.73(3H,s,OMe-6),3.62(1H,m,H-2a),3.58(1H,m,H-5″),3.31(1H,dd,*J*

=15.6,11.3 Hz,H-4b),3.11 (1H,dd,*J*=16.1,4.9 Hz,H-4a),2.47 (1H,m,H-3),2.40 (1H,m,H-2);^{13}C NMR (100 MHz,CD_3OD) δ:149.2 (2C,C-3′ and C-5′),148.3 (C-6),138.7 (C-7),136.6 (C-1′),135.8 (C-4′),134.0 (C-9),128.0 (C-10),117.8 (C-8),112.8 (C-5),107.9 (2C,C-2′ and C-6′),106.0 (C-1″),78.4 (C-3″),75.2 (C-2″),71.1 (C-4″),68.5 (C-2a),67.1 (C-5″),64.2 (C-3a),56.3 (2C,OMe-3′ and OMe-5′),56.1 (OMe-6),47.8 (C-1),45.3 (C-2),39.1 (C-3),33.7 (C-4)。以上数据与文献[6]报道的(-)-5′-甲氧基异落叶松脂醇 9-*O*-β-D-木糖苷[(-)-5′-Methoxyisolariciresinol 9-*O*-β-D-xylopyranoside]一致。

化合物 6 $C_{25}H_{32}O_{10}$,白色粉末。$[\alpha]_D^{20}$ +25° (*c* 0.17,MeOH);ESI-MS *m/z*:515$[M+Na]^+$,1007$[2M+Na]^+$和 491$[M-H]^-$;^{1}H NMR (400 MHz,CD_3OD) δ:7.27 (1H,s,H-2′),7.15 (1H,s,H-5′),6.98 (1H,dd,*J*=8.0,1.8 Hz,H-6′),6.86 (1H,s,H-5),6.85 (1H,s,H-8),4.61 (1H,d,*J*=7.3 Hz,H-1″),4.56 (1H,dd,*J*=9.8,2.4 Hz,H-2a),4.51 (1H,d,*J*=10.9 Hz,H-1),4.24 (1H,t,*J*=10.0 Hz,H-5″),4.22 (2H,m,H-3a),4.14 (1H,m,H-4″),4.06 (1H,t,*J*=9.0 Hz,H-3″),3.99 (1H,t,*J*=8.0 Hz,H-2″),3.79 (3H,s,OMe-6),3.71 (3H,s,OMe-3′),3.66 (1H,dd,*J*=9.8,3.0 Hz,H-2a),3.57 (1H,t,*J*=5.1 Hz,H-5″),3.31 (1H,dd,*J*=15.6,11.3 Hz,H-4b),3.11 (1H,dd,*J*=15.9,4.6 Hz,H-4a),2.47 (1H,m,H-3),2.36 (1H,m,H-2);^{13}C NMR (100 MHz,CD_3OD) δ:148.2 (C-3′),147.3 (C-6),145.8 (C-4′),137.6 (C-1′),136.7 (C-7),134.0 (C-9),128.0 (C-10),117.8 (C-8),116.6 (C-5′),113.9 (C-2′),112.8 (C-5),112.6 (C-6′),106.0 (C-1″),78.4 (C-3″),75.2 (C-2″),71.2 (C-4″),68.5 (C-2a),67.2 (C-5″),64.2 (C-3a),56.1 (OMe-6),55.9 (OMe-3′),47.3 (C-1),45.5 (C-2),39.3 (C-3),33.9 (C-4)。以上数据与文献[6]报道的五味子苷(Schizandriside)一致。

化合物 7 $C_{15}H_{14}O_6$,白色粉末。$[\alpha]_D^{20}$-58° (*c* 0.15,MeOH);ESI-MS *m/z*:289$[M-H]^-$;^{1}H NMR (400 MHz,CD_3OD) δ:6.98 (1H,s,H-2′),6.77 (1H,s,H-6′),6.75 (1H,s,H-5′),6.02 (1H,d,*J*=2.0 Hz,H-6),5.90 (1H,d,*J*=2.0 Hz,H-8),4.81 (1H,br.s,H-2),4.17 (1H,s,H-3),2.81 (1H,dd,*J*=16.5,4.6 Hz,H-4a),2.65 (1H,dd,*J*=16.6,3.5 Hz,H-4b);^{13}C NMR (100 MHz,CD_3OD) δ:156.8 (C-5),156.7 (C-7),156.4 (C-9),144.8 (C-4′),144.2 (C-3′),131.6 (C-1′),118.6 (C-5′),115.6 (C-6′),114.9 (C-2′),99.6 (C-10),95.9 (C-6),95.3 (C-8),78.9 (C-2),66.6 (C-3),28.5 (C-4)。以上数据与文献[8]报道的表儿茶素[(-)-epicatechin)]一致。

化合物 8 $C_{21}H_{20}O_{12}$,黄色针晶(甲醇)。mp. 239~241 ℃,$[\alpha]_D^{20}$-18° (*c* 0.09,MeOH);ESI-MS *m/z*:487$[M+Na]^+$),951$[2M+Na]^+$和 463$[M-H]^-$;^{1}H NMR (400 MHz,CD_3OD) δ:7.56 (2H,m,H-2′ and H-5′),6.84 (1H,d,*J*=8.2 Hz,H-6′),6.40 (1H,d,*J*=2.0 Hz,H-6),6.20 (1H,d,*J*=2.0 Hz,H-8),5.45 (2H,d,*J*=7.2 Hz,H-6″);^{13}C NMR (100 MHz,CD_3OD) δ:177.8 (C-4),161.4 (C-5),156.7 (C-2),156.5 (C-9),148.5 (C-4′),144.1 (C-3′),133.6 (C-3),121.8 (C-5′),121.3 (C-1′),116.4 (C-6′),115.3 (C-2′),104.0 (C-10),101.1 (C-1″),98.8 (C-6),93.7 (C-8),77.6 (C-5″),76.7 (C-3″),74.3 (C-2″),70.1 (C-4″),64.3 (C-7),61.1 (C-6″)。以上数据与文献[8,9]报道的异槲皮苷(Isoquercitrin)一致。

化合物 9 $C_{24}H_{20}O_9$,浅黄色针状结晶(丙酮)。mp. 178~180 ℃,$[\alpha]_D^{20}$-196° (*c* 0.11,MeOH);ESI-MS *m/z*:453$[M+H]^+$,927$[2M+Na]^+$和 451$[M-H]^-$,903$[2M-H]^-$;^{1}H NMR (400 MHz,Me_2CO-d_6) δ:7.10 (1H,d,*J*=2.2 Hz,H-2′),6.83 (1H,d,*J*=8.4 Hz,H-5′),6.72 (1H,dd,*J*=8.4,2.2 Hz,H-6′),6.64 (1H,d,*J*=7.9 Hz,H-6″),6.61 (1H,d,*J*=2.0 Hz,H-2″),6.46 (1H,dd,*J*=7.9,2.0 Hz,H-5″),6.25 (1H,s,H-6),4.89 (1H,br.s,H-2),4.54 (1H,dd,*J*=6.1,2.3 Hz,H-12),4.30 (1H,m,H-3),3.12 (1H,dd,*J*=6.2,6.1 Hz,H-13b),2.93 (1H,m,H-4a),2.88 (1H,m,H-4b),2.85 (1H,dd,*J*=16.2,2.3 Hz,H-13a);^{13}C NMR (100 MHz,CD_3OD) δ:171.2 (C-13),156.6 (C-6),152.5 (C-8),145.4 (C-4″),145.0 (C-3″),144.7 (C-4′),144.1 (C-3′),134.5 (C-1″),131.2 (C-1′),118.4 (C-6′),118.4 (C-6″),115.8 (C-5′),115.8 (C-5″),115.4 (C-10),114.5 (C-2′),114.5 (C-2″),105.2 (C-9),104.5 (C-5),95.8 (C-7),80.7 (C-2),67.5 (C-3),38.8 (C-11),35.7 (C-

12),29.0 (C-4)。以上数据与文献[10]报道的金鸡纳素 Ia (Cinchonain Ia)一致。

化合物 10 $C_{30}H_{48}O_3$,白色粉末。$[\alpha]_D^{20}$ +74° (*c* 0.13, MeOH);ESI-MS *m/z*:479 $[M+Na]^+$,935 $[2M+Na]^+$和455 $[M-H]^-$;^{1}H NMR (400 MHz, CD_3OD) δ:5.46 (1H, m, H-12), 4.17 (1H, m, H-3), 1.29 (6H, s, H-27 and H-29), 1.07 (3H, s, H-23), 1.05 (3H, s, H-24), 1.02 (6H, s, H-25 and H-26), 0.96 (3H, s, H-30);^{13}C NMR (100 MHz, CD_3OD) δ:180.1 (C-28), 144.9 (C-13), 122.4 (C-12), 78.7 (C-3), 55.6 (C-5), 48.4 (C-19), 48.1 (C-9), 46.5 (C-17), 42.3 (C-14), 42.0 (C-8), 39.9 (C-18), 38.7 (C-4), 38.5 (C-1), 38.4 (C-10), 34.3 (C-22), 33.3 (C-29), 33.2 (C-21), 33.1 (C-7), 31.0 (C-20), 29.0 (C-15), 28.3 (C-23), 27.1 (C-2), 26.2 (C-27), 23.9 (C-16), 23.8 (C-30), 23.7 (C-11), 18.8 (C-6), 18.3 (C-24), 17.4 (C-26), 16.8 (C-25)。以上数据与文献[11]报道的熊果酸(Ursolic acid)一致。

化合物 11 $C_{22}H_{22}O$,白色粉末。EI-MS *m/z* (%):302 (55), 287 (100), 209 (18), 197 (12), 105 (20);HR-EI-MS *m/z*:302.1678;^{1}H NMR (400 MHz, $CDCl_3$) δ:7.13 (2H, m, H-5″ and H-7″), 7.12 (2H, m, H-5′ and H-7′), 7.10 (5H, m, H-4, H-4′, H-8′, H-4″ and H-8″), 7.09 (2H, m, H-6′ and H-6″), 7.07 (1H, m, H-3), 6.68 (1H, m, H-6), 4.44 (1H, s, OH), 4.32 (1H, dd, *J* = 7.2, 1.8 Hz, H-1′), 4.05 (1H, dd, *J* = 7.0, 3.6 Hz, H-1″), 1.53 (1H, d, *J* = 7.2 Hz, H-2″), 1.50 (1H, d, *J* = 7.3 Hz, H-2′);^{13}C NMR (100 MHz, $CDCl_3$) δ:151.7 (C-1), 147.1 (C-3″), 145.8 (C-3′), 138.8 (C-4), 132.1 (C-2), 128.6 (C-5′, C-7′), 128.6 (C-5″, C-7″), 127.8 (C-4′, C-8′), 127.8 (C-4″, C-8″), 127.5 (C-3), 126.6 (C-6′), 126.5 (C-5), 126.2 (C-6″), 116.1 (C-6), 44.5 (C-1″), 38.6 (C-1′), 21.3 (C-2′), 23.0 (C-2″)。以上数据与文献[12]报道的 2,5-bis(β-phenylethyl)phenol [2,5-双-(β-苯乙基)苯酚]一致。

参考文献

1 Ma XJ(马小军), Zhao L(赵玲), Du CF(杜程芳), *et al*. Advances in studies on *Gaultheria leucocarpa* var. *yunnanensis* and medicinal plants of *Gaultheria leucocarpa*. *Chin Tradit Herb Drug*(中草药), 2001, 32:945-949.

2 Tan JJ(谭俊杰), Jiang SH(蒋山好), Zhu DY(朱大元). Studies on the chemical constituents of *Pleurospermum lindleyanum*. *Nat Prod Res Dev*(天然产物研究与开发), 2005, 17:267-273.

3 Tetsuo I, Jun-ichi K, Tsunao H, *et al*. An acylated flavonol glycoside from *Lasiobema Japonica*. *Phytochemistry*, 1990, 29:1013-1014.

4 Guo L(郭雷), Gong BQ(龚邦强). Isolation and identification of mPGES-1expression inhibitor from *Craibiodendron yunnanense*. *Nat Prod Res Dev*(天然产物研究与开发), 2008, 20:839-841.

5 Ogawa M, Ogihara Y. Studies on the constituents of *Enkianthus nudipes* V. A new ligan xyloside from the stems. *Chem Pharm Bull*, 1976, 24:2102.

6 Zhang ZZ(张治针), Guo DA(果德安), Li CL(李长龄), *et al*. Studies on the lignan glycosides from *Gaultheria yunnanensis*. *Acta Pharm Sin*(药学学报), 1999, 34:128-131.

7 Ma XJ(马小军), Du CF(杜程芳), Zheng JH(郑俊华), *et al*. Studies on chemical constituents of *Gaultheria leucocarpa* var. *yunnanensis*(Franch.) T. *China J Chin Mater Med*(中国中药杂志), 2001, 26:844-845.

8 Zhou ZH(周志宏), Yang CR(杨崇仁). Chemical constituents of crude green tea, the material of Pu-er tea in Yunnan. *Acta Bot Yunnan*(云南植物研究), 2000, 22:343-350.

9 Gao GY(高光耀), Chen SB(陈四保), Wang LW(王立为), *et al*. Studies on the chemical constituents of *Narrow-raceme meadowrue* (*Thalictrum atriplex*) III. *Chin Tradit Herb Drug*(中草药), 2000, 31:133-136.

10 Chen HF, Tanaka T, Nonaka GI, *et al*. Phenylpropanoid-substituted catechins from *castanopsis hystrix* and structure revision of cinchonains. *Phytochemistry*, 1990, 33:183-187.

11 Wu LJ(吴立军), Xiang T(相婷), Liu TH(刘铁汉), *et al*. NMR study of 3β-(*p*-hydroxy *trans* cinnamoyloxy)-2α-hydroxy-oleanlic acid. *Chin Tradit Herb Drug*(中草药), 1998, 29:367-369.

12 Motoh M, Yoko K, Chiseko W, *et al*. Identification of migrants from nitrile-butadiene rubber gloves. *J Food Hygienic Soc Japan*, 2003, 44:103-109.