苦木茎的化学成分

林清华,徐 健,冯 锋*

(中国药科大学天然药物化学教研室,南京 210009)

摘 要 采用硅胶、ODS 和凝胶等柱色谱方法对苦木(*Picrasma quassioides* Bennet)干燥茎的化学成分进行分离纯化,通过 NMR、MS 等波谱技术鉴定了 17 个化合物,包括 6 个 β-咔巴啉类生物碱:1-methoxycarbonyl-β-carboline (**1**),1-carbamoyl-β-carbolin(**2**),4-methoxy-β-carboline-1-carboxylic acid methyl ester (**3**),1-ethoxycarbonyl-β-carboline(**4**),1-ethyl-β-carboline(**5**),cordysinin C (**6**),5 个铁屎米-6-酮类生物碱:4,5-dimethoxycanthin-6-one (**7**),11-hydroxycanthin-6-one (**8**),5-hydroxycanthin-6-one (**9**),5-hydroxy-4-methoxycanthin-6-one (**10**),canthin-6-one (**11**);2 个铁屎米-5,6-二酮类生物碱:3-methyl-4-methyoxycanthin-5,6-dione(**12**),3-methylcanthin-5,6-dione(**13**);3 个倍半萜类化合物:10α-hydroxycadin-4-en-al (**14**),canangaterpenes III (**15**),15-oxo-T-cadinol(**16**),1 个甾体类化合物 androsta-1,4-diene-3,17-dione (**17**)。其中化合物 **16** 为新的天然产物,化合物 **5**、**6** 和 **14** ~ **17** 为首次从苦木中分离鉴定。

关键词 苦木科;苦木;化学成分;结构鉴定

中图分类号 R969.1 **文献标志码** A **文章编号** 1000 - 5048(2017)06 - 0675 - 05

doi:10.11665/j.issn.1000 - 5048.20170607

引用本文 林清华,徐健,冯锋. 苦木茎的化学成分[J]. 中国药科大学学报,2017,48(6):675 - 679.

Cite this article as: LIN Qinghua, XU Jian, FENG Feng. Chemical constituents from the stems of *Picrasma quassioides* Bennet[J]. *J China Pharm Univ*, 2017, 48(6): 675 - 679.

Chemical constituents from the stems of *Picrasma quassioides* Bennet

LIN Qinghua, XU Jian, FENG Feng*

Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210009, China

Abstract The phytochemical studies on the stems of *Picrasma quassioides* Bennet led to the isolation of seven β-carboline alkaloids (**1-6**), five cantin-6-one alkaloids (**7-11**), two canthin-5, 6-dione (**12**, **13**), three sesquiterpenes (**14-16**), and one steroids (**17**). Their structures were elucidated by the combination of spectroscopic analyses (ESI-MS, ^{1}H NMR and ^{13}C NMR) and the comparisons with the reference. Compound **16** is a new natural product, and this is the first report for compounds **5**, **6**, **14-17** from the species *P. quassioides*.

Key words Simarubaceae; *Picrasma quassioides* Bennet; chemical constituents; structural identification

The study was supported by the National Natural Science Foundation of China (No. 81703382)

苦木[*Picrasma quassioides* (D. Don) Bennet]为苦木科(Simarubaceae)苦木属植物,又称“苦树”、“苦楝树”、“熊胆树”等,以苦味著称,故有“苦树”、“苦胆”之称。在我国主要分布于黄河流域以南各省区,其中广西和广东山区资源比较丰富[1]。其性寒味苦,归肺、大肠经,具有清热祛湿、解毒消肿的功效,用于治疗风热感冒、咽喉肿痛、温热泻痢、湿疹、毒蛇咬伤等疾病[2]。目前,苦木中已分离得到的化学成分主要为 β-咔巴啉类生物碱、铁屎米酮生物碱、苦味素和三萜类[3-5]。现在药理学研究表明苦木具有较好的细胞毒、抗炎、抗菌[6-7]、抗高血压[8]、治疗胃黏膜损伤[9]和抑制血管新生[10]等活性。苦木制剂如苦木注射液、复方苦木消炎片、苦木消炎利胆片等广泛地应用于临床。本

收稿日期 2017-05-12 * **通信作者** Tel:025 - 86185180 E-mail:fengsunlight@126.com

基金项目 国家自然科学基金资助项目(No. 81703382)

研究通过多种现代色谱和波谱技术对该植物的干燥茎的95%乙醇提取液进行系统的化学成分研究,为进一步药效物质基础研究提供依据。

1 材 料

1.1 药材与试剂

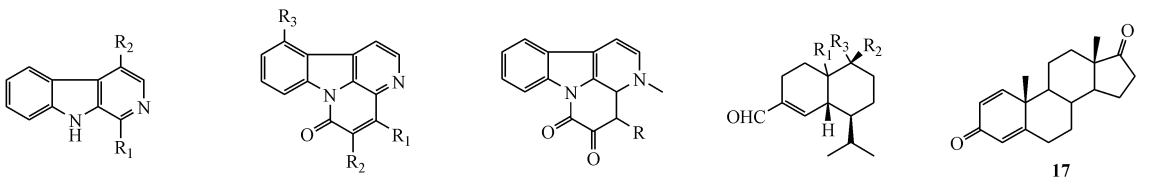
苦木茎,2011年8月采集于中国江西赣州,由中国药科大学中药学院天然药物化学教研室冯锋教授鉴定为 *Picrasma quassioides* (D. Don) Bennet 植物的茎。样品标本存放于中国药科大学天然药物化学教研室内,标本编号为 Piqu-2011JX-A。液相色谱用试剂为市售色谱纯;其他试剂均为市售分析纯。

1.2 仪 器

核磁共振波谱(NMR)使用 DRX-300 型核磁共振波谱仪(德国 Bruker 公司)室温测定,以 TMS 为内标;ESI-MS 使用 Agilent 1100 Series LC/MSD 离子阱质谱仪(美国安捷伦公司)测定;分析型高效液相使用 Shimadzu LC-20 AT 系列,DAD 检测器(日本岛津公司),分析柱为 YMC-pack ODS-A 柱(250 mm×10 mm,S-5 μm,12 nm)。

2 提取和分离

苦木干燥茎 20 kg 用95%乙醇热回流提取(80 L×2 h×2),得总浸膏 465 g。总浸膏经 D101 型大孔吸附树脂柱分离,以乙醇-水梯度洗脱。70%乙醇洗脱部位经硅胶、Sephadex LH-20 和 ODS 等柱色谱反复纯化,得到化合物 **1**(4.5 mg)、**2**(4.2 mg)、**3**(5.0 mg)、**4**(7.6 mg)、**5**(2.6 mg)、**6**(3.1 mg)、**7**(47.2 mg)、**8**(3.8 mg)、**9**(14.7 mg)、**10**(357.2 mg)、**11**(4.7 mg)、**12**(3.2 mg)和 **13**(2.1 mg)。90%乙醇洗脱部位经硅胶、Sephadex LH-20、ODS 和 HPLC 等色谱反复纯化,得到化合物 **14**(7.2 mg)、**15**(2.0 mg)、**16**(3.4 mg)和 **17**(2.2 mg)。



	R_1	R_2
1	$COOCH_3$	H
2	COOH	H
3	$COOCH_3$	OCH_3
4	$COOCH_2CH_3$	H
5	CH_2CH_3	H
6	$CHOHCH_3$	H

	R_1	R_2	R_3
7	OCH_3	OCH_3	H
8	H	H	OH
9	H	OH	H
10	OCH_3	OH	H
11	H	H	H

	R
12	OCH_3
13	H

	R_1	R_2	R_3
14	αH	CH_3	OH
15	βH	CH_3	OH
16	αH	OH	CH_3

Figure 1 Structures of compounds **1-17** from the stems of of *Picrasma quassioides* Bennet

3 结构鉴定

化合物 **1** 白色无定型粉末,5%硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:225 $[M-H]^-$,分子式 $C_{13}H_{10}N_2O_2$。^{1}H NMR (300 MHz,DMSO-d_6) δ:8.48(1H,d,*J* = 5.2 Hz,H-3),8.42(1H,d,*J* = 5.2 Hz,H-4),8.30(1H,d,*J* = 8.0 Hz,H-5),7.61(1H,t,*J* = 7.6 Hz,H-6),7.30(1H,t,*J* = 7.3 Hz,H-7),7.79(1H,d,*J* = 8.3 Hz,H-8),11.65(1H,s,N-H),4.02(3H,s,-OCH_3)。与文献[11]对照,鉴定化合物 **1** 为 1-methoxycarbonyl-β-carboline。

化合物 **2** 淡黄黄色粉末,5%硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:213 $[M+H]^+$,分子式 $C_{12}H_8N_2O_2$。^{1}H NMR(300 MHz,DMSO-d_6) δ:8.39(1H,d,*J* = 5.0 Hz,H-3),8.34(1H,d,*J* = 5.0 Hz,H-4),8.28(1H,d,*J* = 8.0 Hz,H-5),7.57(1H,t,*J* = 7.6 Hz,H-6),7.27(1H,t,*J* = 7.3 Hz,H-7),8.26(1H,d,*J* = 8.1 Hz,H-8),11.65(1H,s,N-H)。与文献[12]对照,鉴定化合物 **2** 为 β-carboline-1-carboxylic acid。

化合物 **3** 黄色针晶,5%硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:257 $[M+H]^+$,分子式 $C_{14}H_{12}N_2O_3$。^{1}H NMR(300 MHz,DMSO-d_6) δ:8.48(1H,s,H-3),8.21(1H,d,*J* = 8.0 Hz,H-5),7.56(1H,t,*J* = 7.7 Hz,H-6),7.29(1H,t,*J* = 7.5 Hz,H-7),7.78(1H,d,*J* = 8.2 Hz,H-8),11.63(1H,s,N-H),3.99(3H,s,4-OCH_3),4.24(3H,s,1′-OCH_3)。与文献[13]对照,鉴定化合物 **3** 为 4-methoxy-β-carboline-1-carboxylic acid

methyl ester。

化合物 **4**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:241[M + H]$^+$,分子式 $C_{14}H_{12}N_2O_2$。^{1}H NMR (300 MHz, DMSO-d_6) δ:8.48(1H,d,J = 4.8 Hz,H-3),8.41(1H,d,J = 4.6 Hz,H-4),8.30(1H,d,J = 8.1 Hz,H-5),7.60(1H,t,J = 7.3 Hz,H-6),7.30(1H,t,J = 7.3 Hz,H-7),7.79(1H,d,J = 8.2 Hz,H-8),11.66(1H,s,N-H),4.50(2H,d,J = 6.9 Hz,1′-CH_2),1.42(3H,t,J = 6.9 Hz,2′-OCH_3)。与文献[14]对照,鉴定化合物 **4** 为 1-ethoxycarbonyl-β-carboline。

化合物 **5**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:219[M + Na]$^+$,分子式 $C_{13}H_{12}N_2$。^{1}H NMR(300 MHz,DMSO-d_6) δ:8.24(1H,d,J = 5.1 Hz,H-3),7.93(1H,d,J = 5.2 Hz,H-4),8.19(1H,d,J = 8.0 Hz,H-5),7.52(1H,t,J = 7.6 Hz,H-6),7.22(1H,t,J = 7.4 Hz,H-7),7.59(1H,d,J = 8.1 Hz,H-8),11.57(1H,s,N-H)。与文献[15]对照,鉴定化合物 **5** 为 1-ethyl-β-carboline。

化合物 **6**　黄色粉末,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:213[M + H]$^+$,分子式 $C_{13}H_{12}N_2O$。^{1}H NMR (300 MHz, $CDCl_3$) δ:8.11(1H,d,J = 5.2 Hz,H-3),8.71(1H,d,J = 5.2 Hz,H-4),8.15(1H,d,J = 8.0 Hz,H-5),7.58(1H,t,J = 8.1 Hz,H-6),7.75(1H,t,J = 8.1 Hz,H-7),7.99(1H,d,J = 8.1 Hz,H-8),5.19(1H,q,J = 6.6 Hz,1′-$CHOHCH_3$),1.71(3H,d,J = 6.0 Hz,2′-$CHOHCH_3$)。与文献[16]对照,鉴定化合物 **6** 为 cordysinin C。

化合物 **7**　淡黄色针晶黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:303[M + Na]$^+$,分子式 $C_{16}H_{12}N_2O_3$。^{1}H NMR (300 MHz, MeOD) δ:8.04(1H,d,J = 5.0 Hz,H-1),8.69(1H,d,J = 5.0 Hz,H-2),8.43(1H,d,J = 8.1 Hz,H-8),7.67(1H,t,J = 8.4 Hz,H-9),7.49(1H,t,J = 8.0 Hz,H-10),8.13(1H,d,J = 7.7 Hz,H-11),4.05(3H,s,4-OCH_3),4.41(3H,s,2′-OCH_3)。与文献[16]对照,鉴定化合物 **7** 为 4,5-dimethoxycanthin-6-one。

化合物 **8**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:235[M − H]$^-$,分子式 $C_{14}H_8N_2O_2$。^{1}H NMR (300 MHz, MeOD) δ:8.10(1H,d,J = 5.0 Hz,H-1),8.79(1H,d,J = 5.1 Hz,H-2),8.14(1H,d,J = 10.0 Hz,H-4),7.00(1H,d,J = 10.0 Hz,H-5),7.98(1H,d,J = 7.8 Hz,H-8),7.58(1H,t,J = 8.0 Hz,H-9),7.02(1H,t,J = 7.9 Hz,H-10),11.07(1H,s,OH)。与文献[17]对照,鉴定化合物 **8** 为 11-hydroxycanthin-6-one。

化合物 **9**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:235[M − Na]$^-$,分子式 $C_{14}H_8N_2O_2$。^{1}H NMR (300 MHz, DMSO-d_6) δ:8.12(1H,d,J = 4.9 Hz,H-1),8.78(1H,d,J = 4.9 Hz,H-2),6.96(1H,s,H-4),8.11(1H,d,J = 7.8 Hz,H-8),7.55(1H,t,J = 8.0 Hz,H-9),7.02(1H,d,J = 7.9 Hz,H-10),7.92(1H,d,J = 7.7 Hz,H-11)。与文献[18]对照,鉴定化合物 **9** 为 5-hydroxycanthin-6-one。

化合物 **10**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:289[M + Na]$^+$,分子式 $C_{15}H_{10}N_2O_3$。^{1}H NMR (300 MHz, DMSO-d_6) δ:8.17(1H,d,J = 5.0 Hz,H-1),8.77(1H,d,J = 5.0 Hz,H-2),8.48(1H,d,J = 8.1 Hz,H-8),7.55(1H,t,J = 7.8 Hz,H-9),7.56(1H,t,J = 7.5 Hz,H-10),8.42(1H,d,J = 7.7 Hz,H-11),4.21(3H,s,4-OCH_3),9.99(1H,br. s,5-OH)。与文献[19]对照,鉴定化合物 **10** 为 5-hydroxy-4-methoxycanthin-6-one。

化合物 **11**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:219[M − H]$^-$,分子式 $C_{14}H_8N_2O$。^{1}H NMR(300 MHz,DMSO-d_6) δ:8.51(1H,d,J = 4.7 Hz,H-1),9.00(1H,d,J = 4.5 Hz,H-2),6.54(1H,d,J = 7.7 Hz,H-4),8.99(1H,t,J = 7.9 Hz,H-5),8.41(1H,d,J = 7.8 Hz,H-8),7.81(1H,t,J = 8.4 Hz,H-9),7.56(1H,t,J = 7.2 Hz,H-10),8.21(1H,d,J = 8.1 Hz,H-11)。与文献[20]对照,鉴定化合物 **10** 为 canthin-6-one。

化合物 **12**　黄色针晶,5% 硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS *m/z*:303[M + Na]$^+$,分子式 $C_{16}H_{12}N_2O_3$。^{1}H NMR (300 MHz, DMSO-d_6) δ:7.51(1H,d,J = 6.6 Hz,H-1),8.05

(1H,d,J = 6.6 Hz,H-2),8.44(1H,d,J = 8.4 Hz,H-8),7.69(1H,t,J = 7.5 Hz,H-9),7.57(1H,d,J = 8.0 Hz,H-10),8.21(1H,d,J = 8.3 Hz,H-11),3.82(1H,s,N-CH_3)。与文献[21]对照,鉴定化合物**12**为3-methyl-4-methyoxycanthin-5,6-dione。

化合物**13** 黄色针晶,5%硫酸乙醇加热显黄色,碘化铋钾反应呈阳性。ESI-MS m/z:273[M + Na]$^+$,分子式 $C_{15}H_{10}N_2O_2$。^{1}H NMR(300 MHz,DMSO-d_6) δ:7.50(1H,d,J = 6.9 Hz,H-1),8.07(1H,d,J = 6.9 Hz,H-2),6.01(1H,s,H-4),8.46(1H,t,J = 8.1 Hz,H-8),7.69(1H,t,J = 7.4 Hz,H-9),7.56(1H,d,J = 7.4 Hz,H-10),8.24(1H,d,J = 7.5 Hz,H-11),3.91(1H,s,N-CH_3)。与文献[22]对照,鉴定化合物**13**为3-methylcanthin-5,6-dione。

化合物**14** 无色针晶,5%硫酸乙醇加热显紫红色。ESI-MS m/z:259[M + Na]$^+$,分子式 $C_{15}H_{24}O_2$。^{1}H NMR(300 MHz,$CDCl_3$) δ:2.09(1H,m,H-2a),2.48(1H,m,H-2b),6.84(1H,s,H-4),2.02(1H,m,H-6),2.24(1H,m,H-11),0.86(3H,d,J = 6.9 Hz,CH_3-12),0.99(3H,d,J = 6.9 Hz,CH_3-13),1.15(3H,s,CH_3-14),9.45(1H,s,CH_3-15)。^{13}C NMR(75 MHz,$CDCl_3$) δ:49.7(C-1),21.4(C-2),22.2(C-3),141.8(C-4),151.6(C-5),41.1(C-6),45.6(C-7),22.1(C-8),41.8(C-9),72.1(C-10),26.2(C-11),15.2(C-12),21.4(C-13),20.5(C-14),194.5(C-15)。与文献[23]对照,鉴定化合物**14**为10α-hydroxycadin-4-en-al。

化合物**15** 无色油状物,5%硫酸乙醇加热显紫红色。ESI-MS m/z:259[M + Na]$^+$,分子式 $C_{15}H_{24}O_2$。^{1}H NMR(300 MHz,$CDCl_3$) δ:2.10(1H,m,H-2a),2.48(1H,dd,J = 5.4,18.0 Hz,H-2b),6.97(1H,d,J = 6.0 Hz,H-4),0.93(3H,d,J = 7.2 Hz,CH_3-12),0.95(3H,d,J = 7.2 Hz,CH_3-13),1.26(3H,s,CH_3-14),9.45(1H,s,CH_3-15)。^{13}C NMR(75 MHz,$CDCl_3$) δ:45.9(C-1),19.5(C-2),22.6(C-3),140.7(C-4),154.8(C-5),36.0(C-6),43.8(C-7),19.5(C-8),34.5(C-9),71.9(C-10),27.2(C-11),15.6(C-12),21.4(C-13),29.5(C-14),193.7(C-15)。与文献[24]对照,鉴定化合物**15**为canangaterpenes III。

化合物**16** 无色油状物,5%硫酸乙醇加热显紫红色。ESI-MS m/z:259[M + Na]$^+$,分子式 $C_{15}H_{24}O_2$。^{1}H NMR(300 MHz,$CDCl_3$) δ:2.09(1H,m,H-2a),2.45(1H,m,H-2b),6.92(1H,s,H-4),2.03(1H,m,H-6),2.23(1H,m,H-11),0.85(3H,d,J = 6.6 Hz,CH_3-12),0.96(3H,d,J = 6.6 Hz,CH_3-13),1.14(3H,s,CH_3-14),9.42(1H,s,CH_3-15)。^{13}C NMR(75 MHz,$CDCl_3$) δ:47.9(C-1),21.5(C-2),22.3(C-3),141.4(C-4),153.1(C-5),39.6(C-6),45.9(C-7),26.7(C-8),40.3(C-9),70.9(C-10),28.9(C-11),15.5(C-12),21.5(C-13),20.2(C-14),194.9(C-15)。与文献[25]对照,鉴定化合物**16**为15-oxo-T-cadinol。

化合物**17** 无色油状物,5%硫酸乙醇加热显蓝灰色。ESI-MS m/z:285[M + H]$^+$,分子式 $C_{19}H_{24}O_2$。^{1}H NMR(300 MHz,$CDCl_3$) δ:7.07(1H,d,J = 10.2 Hz,H-1),6.26(1H,dd,J = 1.8,10.2 Hz,H-2),6.12(1H,s,H-4),0.97(3H,s,CH_3-18),1.28(3H,s,CH_3-19)。^{13}C NMR(75 MHz,$CDCl_3$) δ:155.2(C-1),127.8(C-2),186.2(C-3),124.2(C-4),168.5(C-5),32.6(C-6),31.2(C-7),35.6(C-8),52.4(C-9),43.4(C-10),22.1(C-11),32.6(C-12),47.7(C-13),50.4(C-14),21.9(C-15),35.6(C-16),219.8(C-17),13.8(C-18),18.7(C-19)。与文献[26]对照,鉴定化合物**17**为androsta-1,4-diene-3,17-dione。

参考文献

[1] Zeng JF. *Flora of China*(中国植物志)[M]. Beijing:Science Press,1997,43:7.

[2] Chines Pharmacopoeia Commission. *Chines Pharmacopoeia*(中华人民共和国药典)[S]. Beijng:Chinese Medical Science and Technology Press,2010:186.

[3] Jiao WH. Studies on anti-inflammatory constituents of *Picrasma quassioides* Bennt [D]. Shenyang:Shengyang Pharmaceutical University,2010.

[4] Xu J,Xiao D,Lin QH,*et al*. Cytotoxic tirucallane and apotirucallane triterpenoids from the stems of *Picrasma quassioides*[J]. *J Nat Prod*,2016,**79**:1899 - 1910.

[5] Xu J,Xiao D,Song WW,*et al*. Quassinoids from the stems of *Picrasma quassioides* and their cytotoxic and NO production-inhibitory activities[J]. *Fitoterapia*,2016,**110**:13 - 19.

[6] Zhao F,Gao ZT,Jiao WH,*et al*. *In vitro* anti-inflammatory effects of β-carboline alkaloids, isolated from *Picrasma quassioides*, through inhibition of the iNOS pathway[J]. *Planta Med*,2012,**78**(8):1906 - 1911.

[7] Fan HY, Qi D, Yang MG, *et al*. *In vitro* and *in vivo* anti-inflammatory effects of 4-methoxy-5-hydroxycanthin-6-one, a natural alkaloid from *Picrasma quassioides*[J]. *Phytomedicine*, 2013, **20**(3/4): 319 - 323.

[8] Ma SD, Xie RM, Miao AR, *et al*. The effects of *Picrasma quassioides* on cardiovascular system[J]. *Acta Pharm Sin*(药学学报), 1982, **17**(5): 327 - 330.

[9] Yujiro N, Katsuyosh IM, Koike K, *et al*. Gastric antiulcer components from the woods of *Picrasma quassioides* (Simaroubaceae)[J]. *Nat Med*, 1994, **48**(2): 116 - 121.

[10] Gong GY, Lin QH, Xu J, *et al*. *In vivo* SAR and STR analyses of alkaloids from *Picrasma quassioides* identify 1-hydroxymethyl-8-hydroxy-β-carboline as a novel natural angiogenesis inhibitor[J]. *RSC Adv*, 2016, **6**(12): 9484 - 9494.

[11] Kondo Y, Takemoto T. The structure of a new β-carboline alkaloid from *Picrasma ailanthoides* Planchon[J]. *Chem Pharm Bull*, 1973, **21**(4): 837 - 839.

[12] Lai ZQ, Liu WH, Ip SP, *et al*. Seven alkaloids from *Picrasma quassioides* and their cytotoxic activities[J]. *Chem Nat Compd*, 2014, **50**(5): 884 - 888.

[13] Ohmoto T, Koike K. Studies on the constituents of *Ailanthus altissima* Swingle. III. The alkaloidal constituents[J]. *Chem Pharm Bull*, 1984, **32**(1): 170 - 173.

[14] Chen M, Fan HY, Dai SJ, *et al*. Alkaloids from twigs and leaves of *Picrasma quassioides*[J]. *China Tradit Herb Drugs*(中草药), 2007, **38**(6): 807 - 810.

[15] Lumonadio L, Vanhaelen M. Indole alkaloids from *Hannoa klaineana* roots[J]. *Phytochemistry*, 1984, **23**(2): 453 - 455.

[16] Yang ML, Kuo PC, Hwang TL, *et al*. Anti-inflammatory principles from *Cordyceps sinensis*[J]. *J Nat Prod*, 2011, **74**(9): 1996 - 2000.

[17] Clarke PJ, Jewers K, Jones HF. Crystal and molecular structure of amarorine monohydrate, a new phenolic alkaloid from *Amaroria soulameoides*[J]. *J Chem Soc Perk T*, 1980: 1614 - 1617.

[18] Lassak E V, Polonsky J, Jacquemin H. 5-Hydroxycanthin-6-one from *Simarouba amara*[J]. *Phytochemistry*, 1977, **16**(7): 1126 - 1127.

[19] Kondo Y, Takemoto T. The structure of a new β-carboline alkaloid from *Picrasma ailanthoides* Planchon[J]. *Chem Pharm Bull*, 1973, **21**(4): 837 - 839.

[20] Ohmoto T, Koike K. Studies on the constituents of *Picrasma quassioides* Bennet. II. On the alkaloidal constituents[J]. *Chem Pharm Bull*, 1983, **31**(9): 3198 - 3204.

[21] Ohmoto T, Koike K. Studies on the alkaloids from *Picmsma quassioides* Bennet. VI. Structures of picrasidines N, O, and Q[J]. *Chem Pharm Bull*, 1985, **33**(11): 4901 - 4905.

[22] Ohmoto T, Koike K. Studies on the alkaloids from *Picrasma quassioides* Bennet. V. Structures of picrasidines L, M, and P[J]. *Chem Pharm Bull*, 1985, **33**(9): 3847 - 3851.

[23] Iijima T, Yaoita Y, Kikuchi M. Five new sesquiterpenoids and a new diterpenoid from *Erigeron annuus* (L.) PERS., *Erigeron philadelphicus* L. and *Erigeron sumatrensis* Retz[J]. *Chem Pharm Bull*, 2003, **51**(5): 545 - 549.

[24] Matsumoto T, Nakamura S, Nakashima S, *et al*. Lignandicarboxylates and terpenoids from the flower buds of *Cananga odorata* and their inhibitory effects on melanogenesis[J]. *J Nat Prod*, 2014, **77**(4): 990 - 999.

[25] Wu CL, Chien SC, Wang SY, *et al*. Structure-activity relationships of cadinane-type sesquiterpene derivatives against wood-decay fungi[J]. *Holzforschung*, 2005, **59**(6): 620 - 627.

[26] Chen K, Liu C, Deng L, *et al*. A practical Δ 1-dehydrogenation of Δ 4-3-keto-steroids with DDQ in the presence of TBDMSCl at room temperature[J]. *Steroids*, 2010, **75**(7): 513 - 516.