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麻欠树皮的化学成分研究

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摘　要:对生长于云南省西双版纳州景洪市勐旺乡的麻欠树皮的化学成分进行分离鉴定。通过硅胶、MCI 和 Sephadex LH-20 柱层析、纯化,从麻欠树皮的 90% 甲醇提取物种分离得到 17 个化合物,运用现代波谱技术分别鉴定为:(*S*)-7-甲基十九烷基溴化物(**1**)、1-*O*-*β*-D-葡糖吡喃糖基-(2*S*,3*R*,4*E*,8*E*) -2-[(2-羟基十六酰) 酪胺]-4,8-十八碳二烯基-1,3-二醇(**2**)、machilusmarin(**3**)、邻苯二甲酸二丁酯(**4**)、水杨酸(**5**)、对羟基苯甲酸(**6**)、腺苷(**7**)、alhagidin(**8**)、槲皮素-3-*O*-α-L-阿拉伯吡喃糖苷(**9**)、橙皮甙(橙皮素-7-*O*-芸香糖甙)(**10**)、rhoifoline B(**11**)、zanthoxyline dimethoxy derivative(**12**)、N-两面针碱(**13**)、两面针碱(**14**)、*β*-谷甾醇(**15**)、豆甾醇(**16**)、胡萝卜苷(**17**)。其中化合物 **1** ~ **14** 均为首次从该植物中分离得到。化合物 **1**、**3**、**8**、**10**、**12** 为首次从该属植物中分离得到。

关键词:麻欠;树皮;化学成分;生物碱

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Chemical Constituents from Barks of *Zanthoxylum myriacanthum* var. *pubescens*

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Abstract:The chemical constituents of *Zanthoxylum myriacanthum* var. *pubescens* collected at Mengwang,Jinghong,Yunnan,China were isolated by column chromatography on silica gel,MCI and Sephadex LH-20 and identified by chemical and spectral analyses. Seventeen compounds were finally isolated and purified from barks of *Z. myriacanthum* var. *pubescens*. Their structures were elucidated as 1-bromo-7-methyl-(7*S*)-nonadecane (**1**),1-*O*-*β*-D-glucopyranosyl-(2*S*,3*R*,4*E*,8*E*)-2-[(2-hydroxyhexadecanoyl) amido-]-4,8-octadecadiene-1,3-diol (**2**),machilusmarin (**3**),dibutylphthalate (**4**),salicylic acid (**5**),p-hydroxybenic acid (**6**),adenosine (**7**),alhagidin (**8**),quercetin-3-*O*-α-L-arabinopyranoside (**9**),hesperidin (hesperetin-7-*O*-rutinoside) (**10**),rhoifoline B (**11**),zanthoxyline dimethoxy derivative (**12**),N-nitidine (**13**),nitidine (**14**),sitosterol (**15**),stigmasterol (**16**),daucosterol (**17**). Compounds **1-14** were obtained from this plant for the first time. Compounds **1**,**3**,**8**,**10**,**12** were obtained from this genus for the first time.

Key words:*Zanthoxylum myriacanthum* var. *pubescens*;barks;chemical constituents;alkaloid

麻欠学名为毛大叶臭花椒[*Zanthoxylum myriacanthum* var. *pubescens* Huang (Huang)],为芸香科花椒属植物,是大叶臭花椒的一个变种,分布于云南西双版纳,见于海拔 1400 m 疏或密林中[1]。麻欠是西双版纳地区一种非常典型的民族食用香料,主要用来烧烤、腌肉、煮鱼和做汤[2,3],同时也是一种非常重要的具有治疗消化不良、清热解毒和消肿止痛的民族药[4]。虽然麻欠在西双版纳地区是重要的食用香料和民族药用植物,但是关于傣医所用麻欠树皮药材的化学成分以及生物活性研究却报道很少。因此本研究以生长在中国云南省西双版纳傣族自治州景洪市勐旺乡的麻欠为研究对象,对其化学成分进行研究,分离鉴定了 17 个化合物。分别为:(*S*)-7-甲基十九烷基溴化物(**1**)、1-*O*-*β*-D-葡糖吡喃糖基-(2*S*,3*R*,4*E*,8*E*) -2-[(2-羟基十六酰) 酪胺]-4,8-十八碳二烯基-1,3-二醇(**2**)、machilusmarin(**3**)、邻苯二甲酸二丁酯(**4**)、水杨酸(**5**)、对羟基苯甲酸(**6**)、腺苷(**7**)、alhagidin(**8**)、槲皮素-3-*O*-α-L-阿拉伯吡喃糖苷(**9**)、橙皮甙(橙皮素-7-*O*-芸香糖甙)(**10**)、rhoifoline B(**11**)、zanthoxyline dimethoxy deriv-

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ative(**12**)、N-两面针碱(**13**)、两面针碱(**14**)、β-谷甾醇(**15**)、豆甾醇(**16**)、胡萝卜苷(**17**)。其中化合物**1**~**14**均为首次从该植物中分离得到。化合物**1**、**3**、**8**、**10**、**12**为首次从该属植物中分离得到。

1 仪器与材料

熔点在 XTRC-1 显微熔点测定仪上测定;核磁共振谱用 Bruker AV-400 DRX-500 及 Avance-600 超导核磁共振仪测定,TMS 为内标;EI-MS 用 Waters AutoSpecPremier P776 双聚焦三扇形磁质谱仪测定;柱层析硅胶(200~300 目)及薄板层析硅胶(GF-254)均为青岛海洋化工厂生产;MCI 为日本三菱化学株式会社生产;凝胶材料使用 GE Healthcare 的 Sephadex LH-20,所用有机试剂均为分析纯。

麻欠(*Z. myriacanthum* var. *pubescens*)树皮于 2014 年 8 月采于云南省西双版纳傣族自治州景洪市勐旺乡,并由中国科学院西双版纳热带植物园宋启示研究员鉴定,标本存放于中国科学院西双版纳热带植物园民族药研究组实验室。

2 提取与分离

将麻欠树皮晾干,粉碎,称重得 18 kg。用 90% 甲醇热回流提取 3 次。合并提取液,减压浓缩得甲醇浸膏 2499 g。取 2300 g 浸膏用水搅拌溶解稀释后依次用石油醚、乙酸乙酯、正丁醇萃取,每种溶剂萃取 3 次,得到石油醚萃取物 15 g,乙酸乙酯萃取物 473 g,正丁醇萃取物 975 g。石油醚部分量太少,没有进行分离。乙酸乙酯部分经硅胶柱(200~300 目)分离,以氯仿-甲醇($V_{氯仿}/V_{甲醇}$ = 100∶0、50∶1、20∶1、10∶1、8∶1、4∶1、1∶1)梯度洗脱,得到 B1~B7 七个组分;B1 经反复硅胶柱层析,MCI 和 Sephadex LH20 纯化,得到化合物**1**(6 mg)、**15**(12 mg)、**16**(40 mg);B2 经反复硅胶柱层析,MCI 和 Sephadex LH20 纯化,得到化合物**3**(15 mg)、**11**(5 mg)、**12**(45 mg);B3 经反复硅胶柱层析,MCI 和 Sephadex LH20 纯化,得到化合物**4**(2 mg)、**5**(8 mg)、**6**(6 mg)、**17**(35 mg);B4 经反复硅胶柱层析,MCI 和 Sephadex LH20 纯化,得到化合物**2**(20 mg)、**13**(5 mg)、**14**(10 mg);B5 经反复硅胶柱层析,MCI 和 Sephadex LH20 纯化,得到化合物**7**(8 mg)、**10**(30 mg);B6 经反复硅胶柱层析,MCI 和 Sephadex LH20 纯化,得到化合物**8**(20 mg)。正丁醇部分上大孔树脂分段,分别以体积分数为 30%、60%、90%、100% 比例的甲醇/水溶液梯度洗脱得到四个组分(C1~C4);C2 经反复 MCI 柱层析和 Sephadex LH-20 纯化,得到化合物**8**(20 mg);C3 经反复 MCI 柱层析和 Sephadex LH-20 纯化,得到化合物**9**(2 mg)、**10**(20 mg)。

3 结构鉴定

化合物 1 白色油状固体,分子式为 $C_{20}H_{41}Br$;EI-MS *m/z* 361 [M]$^+$;^{1}H NMR ($CDCl_3$,600 MHz) δ 3.41 (2H,t,*J* = 6.6 Hz,H-1),1.69 (2H,m, *J* = 7.8 Hz,H-2),1.56 (1H,m,H-7),1.29 (18H,m,H-3,11-18),1.25 (8H,m,H-4,5,9,10),1.07 (4H,m,H-6,8),0.88 (3H,t,*J* = 6.6 Hz,H-19),0.84 (3H,d,*J* = 6.0 Hz,7-CH_3);^{13}C NMR ($CDCl_3$,150 MHz) δ 37.1 (C-6,8),33.7 (C-1),33.2 (C-7),32.8 (C-2),32.0 (C-17),30.2 (C-16),30.1 (C-10),29.7 (C-11,C-15),29.4 (C-4),27.1 (C-3),26.7 (C-5,9),22.7 (C-18),19.8 (7-CH_3),14.2 (C-19)。以上数据与文献[5]报道一致,因此确定化合物**1**为(*S*)-7-甲基十九烷基溴化物[1-bromo-7-methyl-(7*S*)-nonadecane]。

化合物 2 白色粉末,mp. 139~197 ℃;分子式为:$C_{40}H_{75}O_9N$;EI-MS *m/z* 713 [M]$^+$;^{1}H NMR (DMSO-d_6,600 MHz) δ 3.79 (2H,dd,*J* = 6.6,10.8 Hz,H-1),4.77 (1H,m,H-2),4.79 (1H,m,H-3),5.60 (1H,dd,*J* = 5.4,13.8Hz,H-4),5.35 (1H,dt,*J* = 5.4,13.2 Hz,H-5),4.52 (1H,dd,*J* = 5.4,11.4 Hz,H-2′),0.85 (6H,t,*J* = 7.2 Hz,2 × CH_3),4.91 (1H,d,*J* = 7.8Hz,H-1″),4.07 (1H,t,*J* = 7.8Hz,H-2″),4.29 (1H,m,H-3″),4.30 (1H,m,H-4″),3.83 (1H,m,H-5″),4.36 (2H,dd,*J* = 6.6,9.6Hz,H-6″),7.52 (1H,d,*J* = 9.6Hz,NH),5.34 (2H,m,H-8,9);^{13}C NMR (DMSO-d_6,150 MHz) δ 173.8 (C-1′),130.3 (C-5),129.9 (C-4),129.7 (C-8),129.4 (C-9),103.5 (C-1″),76.9 (C-3″),76.5 (C-5″),74.1 (C-3),73.5 (C-2″),70.9 (C-1),70.5 (C-2′),70.0 (C-4″),61.0 (C-6″),53.9 (C-2),34.4 (C-3′),32.4 (C-6),32.1 (C-7),31.3 (C-10),31.3~22.1 (C-4′-15′,12-17),25.6 (C-11),14.0 (C-16′,18)。以上数据与文献[6]报道一致,因此确定化合物**2**为 1-*O*-β-D-葡糖吡喃糖基-(2*S*,3*R*,4*E*,8*E*)-2-[(2-羟基十六酰)酪胺]-4,8-十八碳二烯基-1,3-二醇{1-*O*-β-D-glucopyranosyl-(2*S*,3*R*,4*E*,8*E*)-2-[(2-hydroxyhexadecanoyl) amido-]-4,8-octadecadiene-1,3-diol}。

化合物 3 红色粉末,分子式为 $C_{36}H_{40}O_6$;EI-MS *m/z* 568 [M]$^+$;^{1}H NMR (DMSO-d_6,600 MHz) δ 9.75 (1H,s,6-OH,6′-OH),6.96 (1H,d,*J* = 3.0 Hz,H-7,7′),8.44 (1H,d,*J* = 2.4 Hz,H-5),3.47 (2H,d,*J* = 7.2 Hz,H-9,9′),5.06 (1H,t,*J* = 6.6 Hz,H-14,14′),5.31 (1H,t,*J* = 7.2 Hz,H-10,10′),2.05 (2H,m,H-12,12′),2.07 (2H,m,H-13,13′),1.53 (3H,s,H-16,16′),1.59 (3H,s,H-18,18′),1.73 (3H,s,H-17,17′);^{13}C NMR (DMSO-d_6,150 MHz) δ 157.8 (C-1,1′),153.8 (C-6,6′),143.6 (C-8a,8a′),136.8 (C-11,11′),130.9 (C-15,15′),129.5 (C-8,8′),126.0 (C-4a,4a′),124.0 (C-14,14′),121.0 (C-7,7′),120.2 (C-10,10′),116.3 (C-3,3′),109.9 (C-5,5′),39.1 (C-12,12′),27.5 (C-9,9′),26.1 (C-13,13′),25.5 (C-18,18′),17.6 (C-16,16′),16.0 (C-17,17′). 以上数据与文献[7]报道一致,因此确定化合物 **3** 为 machilusmarin。

化合物 4 白色粉末,mp. -35 ℃;分子式为 $C_{16}H_{22}O_4$;EI-MS *m/z* 278 [M]$^+$;^{1}H NMR (CH_3OD,600 MHz) δ 7.70 (2H,dd,*J* = 3.6,6.0 Hz,H-3,6),7.60 (2H,dd,*J* = 3.6,6.0 Hz,H-4,5),4.27 (4H,t,*J* = 6.6 Hz,H-8,8′),1.70 (4H,m,*J* = 6.6 Hz,H-9,9′),1.44 (4H,m,*J* = 7.2 Hz,H-10,10′),0.98 (6H,t,*J* = 7.2 Hz,11,11′);^{13}C NMR (CH_3OD,150 MHz) δ 169.3 (C-7,7′),133.6 (C-1,2),132.4 (C-4,5),129.9 (C-3,6),66.7 (C-8,8′),31.7 (C-9,9′),20.3 (C-10,10′),14.1 (C-11,11′). 以上数据与文献[8]报道一致,因此确定化合物 **4** 为邻苯二甲酸二丁酯(dibutylphthalate)。

化合物 5 黄色针晶(甲醇),mp. 159 ℃;分子式为 $C_7H_6O_3$;EI-MS *m/z* 138 [M]$^+$;^{1}H NMR (MeOD,600 MHz) δ 7.85 (1H,dd,*J* = 7.8,1.8 Hz,H-6),7.44 (1H,t,*J* = 7.8 Hz,H-4),6.91 (1H,d,*J* = 9.6 Hz,H-3),6.87 (1H,t,*J* = 8.4 Hz,H-5);^{13}C NMR (MeOD,150 MHz) δ 173.7 (C-7),163.2 (C-2),136.5 (C-4),131.5 (C-6),120.0 (C-5),118.1 (C-3),114.2 (C-1)。以上数据与文献[9]报道一致,因此确定化合物 **5** 为水杨酸(salicylic acid)。

化合物 6 白色针晶(丙酮),mp. 213 ~ 217 ℃;分子式为 $C_7H_6O_3$;EI-MS *m/z* 138 [M]$^+$;^{1}H NMR (Acetone,600 MHz) δ 7.91 (2H,d,*J* = 8.4 Hz,H-2,6),6.91 (2H,d,*J* = 8.4 Hz,H-3,5);^{13}C NMR (Acetone,150 MHz) δ 167.5 (C-7),162.4 (C-4),132.7 (C-2,6),122.7 (C-1),115.8 (C-3,5)。以上数据与文献[10]报道一致,因此确定化合物 **6** 为对羟基苯甲酸(p-hydroxybenic acid)。

化合物 7 白色粉末,mp. 233 ~ 235 ℃;分子式为 $C_{10}H_{13}O_4N_5$;EI-MS *m/z* 267 [M]$^+$;^{1}H NMR (MeOD,600 MHz) δ 8.30 (1H,s,H-8),8.17 (1H,s,H-2),5.96 (1H,d,*J* = 6.0 Hz,H-1′),4.73 (1H,t,*J* = 6.0 Hz,H-2′),4.31 (1H,dd,*J* = 4.8,2.4 Hz,H-3′),4.16 (1H,dd,*J* = 4.2,2.4 Hz,H-4′),3.87 (1H,dd,*J* = 13.6,2.4 Hz,5′-OH),3.73 (1H,dd,*J* = 13.6,2.4 Hz,H-5);^{13}C NMR (MeOD,150 MHz) δ 156.2 (C-6),152.1 (C-2),148.6 (C-4),140.6 (C-8),120.2 (C-5),89.9 (C-1′),89.9 (C-4′),74.1 (C-2′),71.3 (C-3′),63.0 (C-5′)。以上数据与文献[11]报道一致,因此确定化合物 **7** 为腺苷(adenosine)。

化合物 8 白色粉末,分子式为 $C_{33}H_{44}O_{20}$;EI-MS *m/z* 302 [M]$^+$;^{1}H NMR (DMSO-d_6,600 MHz) δ 3.76 (3H,s,H-7′),9.10 (1H,s,4′-OH),6.90 (3H,m,H-2′,5′,6′),5.49 (1H,m,H-2),3.30 (2H,m,H-3),12.00 (1H,s,5-OH),6.13 (1H,d,*J* = 1.8 Hz,H-8),6.10 (1H,d,*J* = 1.8 Hz,H-6);^{13}C NMR (DMSO-d_6,150 MHz) δ 78.5 (C-2),42.3 (C-3),197.1 (C-4),163.0 (C-5),96.4 (C-6),165.1 (C-7),95.6 (C-8),162.6 (C-9),103.3 (C-10),131.0 (C-1′),114.1 (C-2′),146.4 (C-3′),147.9 (C-4′),112.1 (C-5′),117.8 (C-6′),55.6 (C-7′),99.4 (C-1″),73.0 (C-2″),76.3 (C-3″),70.7 (C-4″),75.5 (C-5″),66.0 (C-6″),100.6 (C-1‴),70.3 (C-2‴),69.6 (C-3‴),72.1 (C-4‴),66.1 (C-5‴),17.9 (C-6‴),95.5 (C-1⁗),68.3 (C-2⁗),68.3 (C-3⁗),70.7 (C-4⁗),69.6 (C-5⁗),55.7 (C-6⁗),以上数据与文献[12]报道一致,因此确定化合物 **8** 为 alhagidin。

化合物 9 黄色粉末,mp. 201 ~ 203 ℃;分子式为 $C_{20}H_{18}O_{11}$;EI-MS *m/z* 434 [M]$^+$;^{1}H NMR (MeOD,600 MHz) δ 7.74 (1H,d,*J* = 1.8 Hz,H-2′),7.58 (1H,dd,*J* = 1.8,8.4 Hz,H-6′),6.87 (1H,d,*J* = 8.4 Hz,H-5′),6.39 (1H,d,*J* = 1.8 Hz,H-8),6.20 (1H,d,*J* = 1.8 Hz,H-6),5.17 (1H,d,*J* = 6.6 Hz,H-1″),3.90 (1H,dd,*J* = 6.6,3.0 Hz,H-2″),3.89 (1H,dd,*J* = 6.6,3.0 Hz,H-4″),3.83 (br,s,H-5″),3.45 (1H,dd,*J* = 3.0,13.8 Hz,H-5″),3.64 (1H,dd,*J* = 8.4,2.4 Hz,H-3″);^{13}C NMR (MeOD,150 MHz) δ 179.5 (C-4),166.7 (C-7),

163.1 (C-5),158.7 (C-9),158.4 (C-2),150.0 (C-4′),146.0 (C-3′),135.6 (C-3),123.0 (C-5′),122.9 (C-1′),117.4 (C-2′),116.2 (C-6′),105.6 (C-10),104.6 (C-1″),99.9 (C-6),94.7 (C-8),74.1 (C-3″),72.9 (C-2″),69.1 (C-4″),67.0 (C-5″)。以上数据与文献[13]报道一致,因此确定化合物**9**为槲皮素-3-*O*-α-L-阿拉伯吡喃糖苷(quercetin-3-*O*-α-L-arabinopyranoside)。

化合物 10 白色粉末,mp. 258 ~ 262 ℃;分子式为 $C_{28}H_{34}O_{15}$;^{1}H NMR (DMSO-d_6,600 MHz) δ 3.77 (3H, s, H-7′),9.31 (1H, s, 4′-OH),6.93 (3H, m, H-2′, 5′, 6′),5.49 (1H, m, H-2),3.38 (2H,m,H-3),12.00 (1H,s,5-OH),6.14 (1H,d, *J* = 1.8 Hz,H-8),6.13 (1H,d, *J* = 1.8 Hz,H-6);^{13}C NMR (DMSO-d_6,150 MHz) δ 197.1 (C-4),165.1 (C-7),163.0 (C-5),162.6 (C-9),148.0 (C-3′),146.4 (C-4′),131.0 (C-1′),117.8 (C-6′),114.1 (C-2′),112.1 (C-5′),103.3 (C-10),96.4 (C-6),95.6 (C-8),78.5 (C-2),55.7 (C-7′),42.3 (C-3). 100.6 (C-1″),99.4 (C-1‴),72.1 (C-4″),70.7 (C-4‴),70.7 (C-5‴),70.3 (C-2″),69.6 (C-3″),68.4 (C-2‴),68.3 (C-3‴),66.1 (C-5″),58.2 (C-6‴),17.9 (C-6″)。以上数据与文献[14]报道一致,因此确定化合物**10**为橙皮甙(橙皮素-7-*O*-芸香糖甙)[hesperidin (hesperetin-7-*O*-rutinoside)]。

化合物 11 红色粉末,分子式为 $C_{21}H_{17}O_5N$;EI-MS *m/z* 363[M]$^+$;^{1}H NMR ($CDCl_3$,600 MHz) δ 8.00 (1H,d,*J* = 9.0 Hz,H-11),7.93 (1H. s,H-7),7.65 (1H,s,H-4),7.60 (1H,s,H-10),7.56 (1H,d,*J* = 8.4 Hz,H-12),7.19 (1H,s,H-1),6.11(2H,s,OCH_2O),4.11 (3H,s,H-9),4.06 (3H,s,H-8),3.99 (3H,s,H-6);^{13}C NMR ($CDCl_3$,150 MHz) δ 164.3 (C-6),153.5 (C-9),149.7 (C-8),147.5 (C-2),147.0 (C-3),135.9 (C-4b),131.8 (C-12a),128.9 (C-10a),123.2 (C-12),121.0 (C-4a),119.1 (C-6a),118.4 (C-11),116.7 (C-10b),108.6 (C-7),104.8 (C-1),102.8 (C-10),102.7 (C-4),101.5 (C-13),56.3 (C-8),56.1 (C-9),41.3 (C-6)。以上数据与文献[15]报道一致,因此确定化合物**11**为 rhoifoline B。

化合物 12 黄色粉末,mp. 206 ~ 208 ℃;分子式为 $C_{20}H_{15}O_4N$;EI-MS *m/z* 333[M]$^+$;^{1}H NMR ($CDCl_3$,400 MHz) δ 9.75 (1H,s,H-6),8.72 (1H,s,H-4),8.35 (1H,d,*J* = 4.0 Hz,H-7),8.34 (1H,d,*J* = 4.8 Hz,H-11),7.59 (1H,d,*J* = 8.8 Hz,H-12),7.27 (1H,d,*J* = 3.2 Hz,H-8),7.26 (1H,s,H-1),6.14 (2H,s,H-13),4.13 (3H,s,H-14),4.06 (3H,s,H-15);^{13}C NMR ($CDCl_3$,100 MHz) δ 149.6 (C-9),148.4 (C-3),148.2 (C-2),146.5 (C-6),145.1 (C-10),139.9 (C-4b),129.7 (C-12a),129.1 (C-4a),128.0 (C-6a),127.0 (C-12),121.8 (C-10a),120.0 (C-10b),118.6 (C-8),118.3 (C-7),118.2 (C-11),104.3 (C-1),102.1 (C-4),101.3 (C-13),61.9 (C-15),56.7 (C-14)。以上数据与文献[16]报道一致,因此确定化合物**12**为 zanthoxyline dimethoxy derivative。

化合物 13 橘黄色粉末,mp. 227 ~ 279 ℃;分子式为 $C_{20}H_{15}O_4N$;EI-MS *m/z* 333[M]$^+$;^{1}H NMR ($CDCl_3$,600 MHz) δ 9.25 (1H,s,H-6),8.71 (1H,s,H-4),8.31 (1H,d,*J* = 9.0 Hz H-11),7.90 (1H,s,H-7),7.85 (1H,d,*J* = 9.0 Hz H-12),7.40 (1H,s,H-10),7.27 (1H,s,H-1),6.14 (2H,s,H-13),4.17 (3H,s,H-14),4.10 (3H,s,H-15);^{13}C NMR ($CDCl_3$,150 MHz) δ 152.9 (C-6),149.7 (C-9),149.7 (C-8),148.4 (C-3),148.2 (C-2),140.6 (C-10a),129.6 (C-12a),129.2 (C-4b),128.8 (C-12),126.6 (C-10b),122.2 (C-6a),119.9 (C-11),118.2 (C-4a),107.3 (C-7),104.4 (C-10),102.2 (C-1),101.6 (C-4),101.3 (C-13),56.2 (C-14),56.1 (C-15)。以上数据与文献[17]报道一致,因此确定化合物**13**为 N-两面针碱(N-nitidine)。

化合物 14 黄色粉末,mp. 281 ~ 283 ℃;分子式为 $C_{21}H_{18}O_4N$;EI-MS *m/z* 348[M]$^+$;^{1}H NMR (DMSO-d_6,600 MHz) δ 9.81 (1H,s,H-6),8.89 (1H,d,*J* = 3.6Hz,H-11),8.30 (1H,s,H-10),8.29 (1H,s,H-4),8.28 (1H,d,*J* = 3.6Hz,H-12),7.89 (1H,s,H-7),7.77 (1H,s,H-1),6.33 (2H,s,H-13),4.87 (3H,s,H-14),4.21 (3H,s,H-16),4.03 (3H,s,H-15);^{13}C NMR (DMSO-d_6,150 MHz) δ 158.4 (C-9),151.7 (C-8),151.5 (C-6),149.0 (C-2),148.6 (C-3),132.8 (C-4b),132.7 (C-12a),132.3 (C-10a),130.2 (C-12),124.3 (C-10b),120.1 (C-4a),119.6 (C-6a),119.4 (C-11),108.9 (C-7),105.9 (C-1),104.7 (C-4),103.4 (C-10),102.9 (C-13),57.4 (C-16),56.5 (C-15),51.6 (C-14)。以上数据与文献[18]报道一致,因此确定化合物**14**为两面针碱(nitidine)。

化合物 15 白色针状结晶(氯仿),mp. 139 ~

140 ℃,分子式为 $C_{29}H_{50}O$,EI-MS *m/z* 414 [M]$^+$,其^{1}H NMR 和^{13}C NMR 图谱与-谷甾醇的标准图谱完全一致,TLC 上的斑点位置及显色与-谷甾醇标准品的相同,且与标准品混合熔点不下降,因此确定化合物 **15** 为-谷甾醇(sitosterol)。

化合物 16 白色片状结晶(氯仿),mp. 169 ~ 170 ℃,分子式为 $C_{29}H_{48}O$;EI-MS *m/z* 412 [M]$^+$;其在 TLC(展开系统:$V_{氯仿}/V_{丙酮}$:15∶1 10∶1 8∶1;$V_{石油醚}/V_{丙酮}$:20∶1 10∶1 6∶1)上的斑点位置及显色与豆甾醇标准品的相同,且与标准品混合熔点不下降,因此确定化合物 **16** 为豆甾醇(stigmasterol)。

化合物 17 白色粉末(氯仿),mp. 283 ~ 284 ℃,分子式为 $C_{35}H_{60}O_6$,其^{1}H NMR 和^{13}C NMR 图谱与-胡萝卜苷的标准图谱完全一致,TLC 上的斑点位置及显色与-胡萝卜苷标准品的相同,且与标准品混合熔点不下降,所以确定化合物 **17** 为-胡萝卜苷(daucosterol)。

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