

DOI: 10.11931/guihaia.gxzw201404039

吴相雷,熊筱娟,吴志军,等. 云南兔儿风的五环三萜类化学成分研究[J]. 广西植物,2015,35(1):109–114

Wu XL, Xiong XJ, Wu ZJ, et al. The pentacyclic triterpene of *Ainsliaea yunnanensis*[J]. *Guihaia*, 2015, 35(1):109–114

# 云南兔儿风的五环三萜类化学成分研究

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**摘要:** 以采自云南省楚雄自治州楚雄市的云南兔儿风(*Ainsliaea yunnanensis*)干燥地上部分为研究对象,应用现代色谱手段(硅胶柱色谱、ODS 柱色谱、Sephadex LH-20 凝胶柱色谱、制备液相及制备薄层色谱等),从云南兔儿风植物中分离单体化合物,运用光谱分析技术(MS、<sup>1</sup>H-NMR、<sup>13</sup>C-NMR、DEPT、COSY、HSQC、HMBC、ROSEY)鉴定其化学结构,对云南兔儿风的化学成分进行研究,为兔儿风属植物研究及植物开发利用提供一定的物质基础。结果表明:从云南兔儿风乙醇提取物中共分离得到了 11 个五环三萜类化合物,分别鉴定为  $\alpha$ -香树脂醇乙酸酯(1)、羽扇豆醇乙酸酯(2)、9,12-二烯乌苏烷乙酸酯(3)、 $\alpha$ -香树脂酮(4)、羽扇豆烯酮(5)、蛇菰素 B(6)、降香萜醇乙酸酯(7)、齐墩果烷-11-羰基-12-烯-3-醇棕榈酸酯(8)、12-烯基白桦脂醇(9)、西米杜鹃醇(10)、二十烷酸羽扇豆醇乙酸酯(11)。其中,化合物 1~6, 9~11 均为首次从该植物中分离得到。通过对云南兔儿风化学成分进行深入研究,明确其主要的活性成分,阐明云南兔儿风药用植物中抗炎活性物质基础,为相关的新药科研工作及产品开发提供重要的科学依据。

**关键词:** 云南兔儿风; 化学成分; 五环三萜

中图分类号: Q946.8 文献标识码: A 文章编号: 1000-3142(2015)01-0109-06

## The pentacyclic triterpene of *Ainsliaea yunnanensis*

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**Abstract:** Plants of *Asteraceae* are well known for containing biologically active chemical constituents. Within this family, the genus *Ainsliaea* comprises 70 species, 48 of which are indigenous to China. Many *Ainsliaea* species are used in Chinese folk medicine for various indications. *A. yunnanensis*, *Ainsliaea* compositae plant, is born in 1 700–2 700 m above sea level of forests, forest margins, or mountain grass, mainly distributed in Yunnan, Sichuan and other places. And it is used in clinic to treat injuries, fractures, rheumatism bones and muscles pain, indigestion, sores and insect product disease. The latest pharmacological research revealed that *A. yunnanensis* had wide range of biological activities, such as antioxidant, antitumor, antiinflammatory properties. To explore the material basis of antiinflammatory activities and establish the basis for exploitation and utilization for the future, we had conducted a phytochemical investigation on the EtOH extract of the aerial parts of *A. yunnanensis*. So far, several sesquiterpenes, triterpenes and flavonoids, had been isolated from this genus. For example, arbutin, friedelin, friedelan-3 $\beta$ -ol, fernenol from *A. frans*

收稿日期: 2014-05-16 修回日期: 2014-12-19

基金项目: 国家“重大新药创制”科技重大专项(2009ZX09502-013); 2013 年江西省学位与研究生教育教学改革研究项目(JXYJG-2013-112)。

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Champ. 8- $\alpha$ -hydroxy-11 $\alpha$ , 13-dihydrozaluzanin C, 3-O- $\beta$ -D-glucosaluzanin C from *A. fragrans* Champ. Acaciin, luteolin, luteolin-7-O- $\beta$ -D-glucoside, chrysoeriol-7-O- $\beta$ -D-glucoside, apigenin-7-O- $\beta$ -D-glucoside from *A. bonatii Beauverd.* 3,5-dicaffeoylquinic acid and 4,5-dicaffeoylquinic acid from *Ainsliaea fragrans* Champ. Ainsliaea A, ainsliaea B, zaluzanin C, 3-O-(9Z, 12Z, 15Z-octadecatrienoyl) glycerol, 3-O-(9Z, 2Z-octadecatrienoyl) glycerol and glueozaluzanin C from *A. acerifolia* SchBip and *A. dissecta* Franch Et Sav. Ainsliolide A, ainsliolide B, taraxinic acid, taraxinic acid-14-O- $\beta$ -D-glucopyranoside from *Ainsliaea acerifolia* var *subapoda*. Three dimeric sesquiterpene lactones were identified as ainsliadimer A, ainsliadimer B, ainsliadimer C from *A. macrocephal*, and one dimeric sesquiterpene lactone was identified as gochnatiolide A from *A. henryi*, two triple sesquiterpene lactones (ainsliatriimer A, ainsliatriimer B) from *A. fulvioides*. In the dissertation, we investigated the chemical constituents of *A. yunnanensis* systematically, the plant material was collected in Chuxiong Yi Autonomous Prefecture, Yunnan Province, China and identified by Prof. Tan Ceming, plant herbarium of Jiangxi Province. Eleven pentacyclic triterpene compounds were isolated and identified as  $\alpha$ -amyrin acetate (**1**), lupenyl acetate (**2**), 3 $\beta$ -acetoxy-9(11):12-diene-ursan (**3**),  $\alpha$ -amyrenone (**4**), lupenone (**5**), balanophorin B (**6**), bauerenyl acetate (**7**), 3 $\beta$ -hydroxy-11-oxo-olean-12-enyl palmitate (**8**), lupa-12, 20(29)-dien-3 $\beta$ , 28-diol (**9**), simiarenol (**10**), lup-20(29)-ene-3 $\beta$ -yl eicosanoate (**11**). These compounds were isolated from *A. yunnanensis* by silica gel, ODS, Sephadex LH-20, preparative HPLC and preparative TLC and were identified by spectral analysis (MS, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, DEPT, COSY, HSQC, HMBC, ROSEY). Compounds **1-6, 9-11** were isolated from *A. yunnanensis* for the first time. The genus *Ainsliaea* has been commonly used as crude material of traditional Chinese medicine for a long time, but the study of the genus was sparse, therefore this study would accumulate data for chemical constituents research of the genus.

**Key words:** *Ainsliaea yunnanensis*; chemical constituents; pentacyclic triterpene

云南兔儿风 (*Ainsliaea yunnanensis*) 是菊科兔儿风属植物, 主要分布于云南、四川等地, 生于海拔 1 700~2 700 m 的林下、林缘或山坡草地上 (中国植物志编辑委员会, 1996)。民间主要用于跌打损伤, 骨折, 风湿筋骨痛, 消化不良, 疮积, 虫积等 (江苏新医学院, 1977)。云南兔儿风的粗提物具有较好的抗氧化, 抗肿瘤, 抗炎活性 (王蓉等, 2013)。兔儿风属植物中含有大量的倍半萜, 三萜, 黄酮类等化学成分 (田亮, 2004)。为进一步阐明兔儿风属植物的化学成分, 本课题组对文献报道较少的云南兔儿风的化学成分进行研究, 从中分离得到 11 个五环三萜类化合物, 分别鉴定为  $\alpha$ -香树脂醇乙酸酯 ( $\alpha$ -amyrin acetate, **1**), 羽扇豆醇乙酸酯 (lupenyl acetate, **2**), 9, 12-二烯乌苏烷乙酸酯 (3 $\beta$ -acetoxy-9(11):12-diene-ursan, **3**),  $\alpha$ -香树脂酮 ( $\alpha$ -amyrenone, **4**), 羽扇豆烯酮 (lupenone, **5**), 蛇菰素 B (balanophorin B, **6**), 降香萜醇乙酸酯 (bauerenyl acetate, **7**), 齐墩果烷-11-蒾基-12-烯-3-醇棕榈酸酯 (3 $\beta$ -hydroxy-11-oxo-olean-12-enyl palmitate, **8**), 12-烯基白桦脂醇 (lupa-12, 20(29)-dien-3 $\beta$ , 28-diol, **9**), 西米杜鹃醇 (simiarenol, **10**), 二十烷酸羽扇豆醇乙酸酯 (lup-20(29)-ene-3 $\beta$ -yl eicosanoate, **11**)。化合物 **1-6, 9-11** 均为首次从该植物中分离得到。

## 1 仪器与材料

### 1.1 仪器

Bruker Avance 600 核磁共振仪; Waters Q-Tof Micro 质谱仪; 正相硅胶 (100~200 目, 200~300 目) 及正相硅胶板, 均为烟台江友硅胶开发公司生产, ODS, C18 反相硅胶及反相硅胶板, 均为 Merck 公司生产, Sephadex LH-20 (40~70  $\mu$ m), Pharmacia Biotech 公司生产, 溶剂为分析纯 (国药集团化学试剂有限公司生产)。

### 1.2 材料

药材采自云南省楚雄自治州楚雄市, 由江西省九江市植物标本馆的谭策铭教授鉴定为兔儿风属植物云南兔儿风 (*Ainsliaea yunnanensis*) 全草。

## 2 方法与结果

### 2.1 提取和分离

云南兔儿风干燥全草 20 kg, 用 80% 乙醇加热回流提取 3 次, 合并提取液, 加热回收乙醇, 提取液分别用石油醚、乙酸乙酯和正丁醇各萃取 3 次, 合并萃取液浓缩得石油醚萃取物 (240 g)、乙酸乙酯萃取物 (350 g) 和正丁醇萃取物 (450 g)。

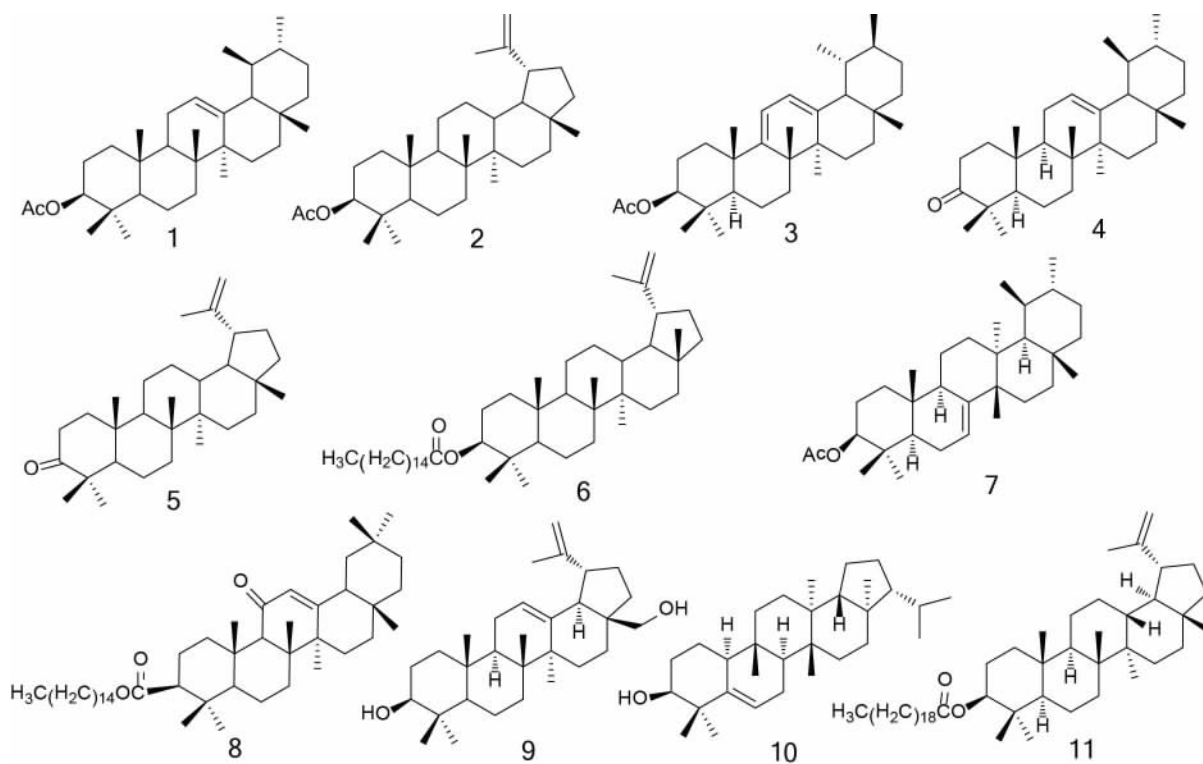


图 1 化合物 1~11 结构式

Fig. 1 Structure of compounds 1-11

石油醚萃取物(240 g)经硅胶柱色谱梯度洗脱(石油醚:乙酸乙酯=500:1~50:1),合并相同组分,得到 5 个流分(Fr.1-5),Fr.1 经正相硅胶柱色谱梯度洗脱(石油醚-乙酸乙酯 500:1~100:1)得到化合物 1(1.0 g)和 2(240 mg),Fr.2 经凝胶柱 SephadexLH-20(二氯甲烷-甲醇 1:1)洗脱得到化合物 3(48 mg)和 Fr.2.1,Fr.2.1 进一步用硅胶柱色谱分离得到化合物 4(80 mg),Fr.3 经凝胶柱 SephadexLH-20(二氯甲烷-甲醇 1:1)洗脱得到化合物 5(70 mg)和 Fr.3.1,Fr.3.1 经正相硅胶(石油醚-乙酸乙酯 300:1~50:1)梯度洗脱得到化合物 6(40 mg)和化合物 7(100 mg),Fr.4 经凝胶柱 SephadexLH-20(二氯甲烷-甲醇 1:1)洗脱得到化合物 8(39)mg 和 Fr.4.1,Fr.4.1 进一步经正相硅胶柱(石油醚-乙酸乙酯 200:1~50:1)、ODS 色谱柱(甲醇-水 9:1~1:0)梯度洗脱得到化合物 9(50 mg)及化合物 10(15 mg),Fr.5 经凝胶柱 SephadexLH-20(二氯甲烷-甲醇 1:1 洗脱)得到 Fr.5.1 和 Fr.5.2。Fr.5.1 经 ODS 色谱柱(甲醇-水 9:1~1:0)梯度洗脱得到化合物 11(10 mg)。

## 2.2 结构鉴定

化合物 1 白色针晶( $\text{CDCl}_3$ ), mp = 231~232

$^{\circ}\text{C}$ ,  $\text{IR}_{\text{Vmax}}$  (KBr)  $\text{cm}^{-1}$ : 2 980, 2 975, 1 735, 1 455, 1 397, 1 366, 1 243, 1 003, 967. 分子式为  $\text{C}_{32}\text{H}_{52}\text{O}_2$ , ESI-MS  $m/z$ : 469  $[\text{M}]^+$ ,  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.78, 0.79, 0.86, 0.87, 0.93, 0.98, 1.00, 1.06 (各 3H,  $\text{CH}_3 \times 8$ ), 2.03 (3H, s, H-2'), 4.49 (1H, dd,  $J = 10.2, 5.4$  Hz, H-3), 5.11 (1H, t,  $J = 3.6$  Hz, H-12);  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 15.7 (t, C-25), 16.7 (q, C-26), 16.9 (q, C-24), 17.5 (q, C-29), 18.3 (t, C-6), 21.3 (q, C-2'), 21.4 (q, C-30), 23.2 (q, C-27), 23.4 (t, C-11), 23.6 (t, C-2), 26.6 (t, C-16), 28.1 (q, C-23), 28.1 (q, C-28), 28.7 (t, C-15), 31.3 (t, C-21), 32.9 (t, C-7), 33.7 (s, C-17), 36.8 (s, C-10), 37.7 (s, C-4), 38.5 (t, C-1), 39.6 (d, C-20), 39.7 (d, C-19), 40.1 (s, C-8), 41.5 (t, C-22), 42.1 (s, C-14), 47.7 (d, C-9), 55.3 (d, C-5), 59.1 (d, C-18), 81.0 (d, C-3), 124.3 (d, C-12), 139.6 (d, C-13), 171.0 (s, C-1'). 分析以上波谱数据,与文献(陈书红等,2006)数据基本一致,因此鉴定化合物 1 为  $\alpha$ -香树脂醇乙酸酯。

化合物 2 白色粉末( $\text{CDCl}_3$ ), mp = 217~218  $^{\circ}\text{C}$ ,  $\text{IR}_{\text{Vmax}}$  (KBr)  $\text{cm}^{-1}$ : 2 960, 1 735, 1 430, 1 380, 1 246, 1 005, 880. 分子式为  $\text{C}_{32}\text{H}_{52}\text{O}_2$ , ESI-MS  $m/z$ :

z: 469 [M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.72 (3H, s, H-28), 0.79 (3H, s, H-24), 0.80 (3H, s, H-23), 0.88 (3H, s, H-25), 0.94 (3H, s, H-27), 0.98 (3H, s, H-26), 1.63 (3H, s, H-30), 1.99 (3H, s, H-2'), 4.51 (1H, br s, H-3), 4.63 (2H, br s, H-29); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 14.4 (q, C-27), 15.9 (q, C-26), 16.1 (q, C-25), 16.4 (q, C-24), 17.9 (q, C-28), 18.1 (t, C-6), 19.2 (q, C-30), 20.9 (t, C-11), 21.5 (q, C-2'), 23.6 (t, C-2), 25.0 (t, C-12), 27.4 (t, C-15), 27.8 (q, C-23), 29.7 (t, C-21), 34.1 (t, C-7), 35.5 (t, C-16), 37.0 (s, C-10), 37.6 (t, C-1), 37.9 (d, C-13), 38.4 (s, C-4), 39.9 (t, C-22), 40.8 (d, C-8), 42.8 (s, C-14), 42.9 (s, C-17), 47.9 (C-18, d), 48.2 (d, C-19), 50.3 (d, C-9), 55.3 (d, C-5), 81.2 (d, C-3), 109.2 (t, C-29), 150.9 (s, C-20), 171.3 (s, C-1'). 分析以上波谱数据, 与文献(刘金磊等, 2012)数据基本一致, 因此鉴定化合物 2 为羽扇豆醇乙酸酯。

**化合物 3** 白色固体 (CDCl<sub>3</sub>), mp = 178 ~ 179 °C, IR<sub>v<sub>max</sub></sub> (KBr) cm<sup>-1</sup>: 2 960, 1 735, 1 679, 1 275, 1 050, 990. 分子式为 C<sub>32</sub>H<sub>50</sub>O<sub>2</sub>, ESI-MS m/z: 467 [M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.76, 0.78, 0.79, 0.85, 0.86, 0.96, 0.99, 1.12 (各 3H, CH<sub>3</sub> × 8), 1.98 (3H, s, H-2'), 4.50 (1H, dd, J = 11.8, 4.8 Hz, H-3), 5.49 (1H, d, J = 5.8 Hz, H-12), 5.55 (1H, d, J = 6.0 Hz, H-11); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 15.9 (q, C-29), 16.8 (q, C-24), 17.4 (q, C-25), 18.2 (t, C-6), 21.0 (q, C-30), 21.5 (q, C-2'), 23.7 (q, C-26), 24.3 (t, C-2), 25.4 (q, C-27), 25.6 (t, C-16), 28.2 (q, C-23), 28.7 (q, C-28), 29.2 (t, C-15), 31.9 (t, C-21), 32.1 (t, C-7), 34.6 (s, C-17), 36.8 (t, C-1), 37.9 (s, C-10), 38.6 (s, C-4), 39.1 (d, C-19), 39.6 (d, C-20), 40.6 (s, C-8), 41.4 (t, C-22), 43.1 (s, C-14), 51.2 (d, C-5), 55.4 (d, C-18), 80.5 (d, C-3), 115.9 (d, C-11), 120.7 (d, C-12), 147.2 (s, C-13), 153.9 (s, C-9), 171.6 (s, C-1'). 分析以上波谱数据, 与文献(Nguyen *et al.*, 2002)数据基本一致, 因此鉴定化合物 3 为 9,12-二烯乌苏烷乙酸酯。

**化合物 4** 白色粉末 (CDCl<sub>3</sub>), mp = 177 ~ 178 °C, IR<sub>v<sub>max</sub></sub> (KBr) cm<sup>-1</sup>: 2 980, 2 975, 1 730, 1 631, 1 397, 1 366, 1 243, 982, 965. 分子式为 C<sub>30</sub>H<sub>48</sub>O, ESI-MS m/z: 425 [M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.78 (3H, br s, H-29), 0.84 (3H, s, H-28), 0.99 (3H, s, H-30), 1.03 (3H, s, H-26), 1.04

(3H, s, H-24), 1.08 (3H, s, H-25), 1.09 (3H, s, H-27), 1.11 (3H, s, H-23), 5.12 (1H, t, J = 4.2 Hz, H-12); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 15.4 (q, C-25), 16.8 (q, C-26), 17.4 (q, C-29), 19.6 (t, C-6), 21.3 (q, C-30), 21.4 (q, C-24), 23.1 (q, C-27), 23.5 (t, C-11), 26.5 (t, C-16), 28.4 (q, C-23), 28.7 (t, C-15), 28.7 (q, C-28), 31.2 (t, C-21), 32.4 (t, C-7), 33.7 (s, C-17), 34.1 (t, C-2), 36.6 (s, C-10), 39.4 (t, C-1), 39.5 (d, C-19), 39.6 (d, C-20), 39.9 (s, C-8), 41.4 (t, C-22), 42.2 (s, C-14), 46.9 (d, C-9), 47.3 (s, C-4), 55.2 (d, C-5), 59.1 (d, C-18), 217.5 (d, C-3), 124.1 (d, C-12), 139.7 (s, C-13)。分析以上波谱数据, 与文献(郭君良等, 2011)数据基本一致, 因此鉴定化合物 4 为 α-香树脂酮。

**化合物 5** 淡黄色油状物 (CDCl<sub>3</sub>), mp = 175 ~ 176 °C, IR<sub>v<sub>max</sub></sub> (KBr) cm<sup>-1</sup>: 2 940, 1 710, 1 430, 1 380, 995, 880. 分子式为 C<sub>30</sub>H<sub>48</sub>O, ESI-MS m/z: 425 [M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.78 (3H, s, H-28), 0.91 (3H, s, H-25), 0.93 (3H, s, H-27), 1.00 (3H, s, H-24), 1.05 (3H, s, H-26), 1.06 (3H, s, H-23), 1.66 (3H, s, H-30), 4.56 (1H, br s, H-29b), 4.67 (1H, br s, H-29a); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 14.4 (q, C-27), 15.7 (q, C-26), 15.9 (q, C-25), 18.0 (q, C-28), 19.3 (t, C-6), 19.6 (q, C-30), 21.0 (q, C-24), 21.4 (t, C-11), 25.9 (t, C-12), 26.8 (t, C-15), 26.9 (q, C-23), 29.8 (t, C-21), 33.5 (t, C-7), 34.1 (t, C-2), 35.8 (t, C-16), 36.8 (s, C-10), 38.1 (d, C-13), 39.9 (t, C-1), 39.9 (t, C-22), 40.7 (s, C-8), 42.8 (s, C-17), 42.9 (s, C-14), 47.3 (s, C-4), 48.1 (d, C-19), 48.2 (d, C-18), 49.8 (d, C-9), 54.9 (d, C-5), 109.3 (t, C-29), 150.8 (s, C-20), 218.0 (s, C-3)。分析以上波谱数据, 与文献(赵奎君等, 2001)数据基本一致, 因此鉴定化合物 5 为羽扇豆烯酮。

**化合物 6** 无定形粉末 (CDCl<sub>3</sub>), mp = 69 ~ 70 °C, IR<sub>v<sub>max</sub></sub> (KBr) cm<sup>-1</sup>: 2 914, 2 850, 1 730, 1 641, 1 471, 1 381, 1 265, 1 173, 980. 分子式为 C<sub>46</sub>H<sub>80</sub>O<sub>2</sub>, ESI-MS m/z: 665 [M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.78 (3H, s, H-28), 0.85 (3H, s, H-16), 0.93 (3H, s, H-24), 1.02 (3H, s, H-26), 1.67 (3H, s, H-30), 2.29 (2H, t, J = 7.8 Hz, H-2'), 4.45 (1H, dd, J = 11.4, 5.4 Hz, H-3), 4.56 (1H, s, H-29b), 4.68 (1H, s, H-29a); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 14.1 (q, C-16'), 14.5 (q, C-27), 16.0 (q, C-24), 16.2

(q, C-26), 16.6 (q, C-25), 18.0 (t, C-6), 18.2 (q, C-28), 19.3 (q, C-30), 21.0 (t, C-11), 22.7 (t, C-15'), 23.8 (t, C-2), 25.0 (t, C-3'), 25.2 (t, C-12), 27.5 (t, C-15), 28.0 (q, C-23), 29.2-29.9 (t, C-4'-13'), 29.9 (t, C-21), 31.9 (t, C-14'), 34.1 (t, C-2'), 34.2 (t, C-7), 35.6 (t, C-16), 37.1 (d, C-13), 37.8 (t, C-1), 38.1 (s, C-10), 38.4 (s, C-4), 40.0 (t, C-22), 40.9 (s, C-8), 42.8 (s, C-14), 43.0 (s, C-17), 48.0 (d, C-19), 48.3 (d, C-18), 50.4 (d, C-9), 55.4 (d, C-5), 80.6 (d, C-3), 109.3 (t, C-29), 150.9 (s, C-20), 174.3 (s, C-1'). 分析以上波谱数据, 与文献(戴忠等, 2005)数据基本一致, 因此鉴定化合物 6 为蛇菰素 B。

**化合物 7** 白色晶体 (CDCl<sub>3</sub>), mp = 293 ~ 294 °C, IR<sub>vmax</sub> (KBr) cm<sup>-1</sup>: 2 910, 2 845, 1 710, 1 650, 1 370, 1 007, 950. 分子式为 C<sub>32</sub>H<sub>52</sub>O<sub>2</sub>, ESI-MS m/z: 469[M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, Pyridine) δ: 0.73, 0.75, 0.82, 0.91, 0.91, 0.94, 0.99, 1.00 (各 3H, s, CH<sub>3</sub> × 8), 1.01 (3H, d, J = 6.4 Hz, H-29), 2.07 (3H, s, H-2'), 4.67 (1H, dd, J = 11.7, 4.1 Hz, H-3), 5.41 (1H, br s, H-7); <sup>13</sup>C-NMR (150 MHz, Pyridine) δ: 12.6 (q, C-25), 15.4 (q, C-23), 16.5 (t, C-15), 20.6 (q, C-30), 22.1 (q, C-27), 22.3 (q, C-26), 23.2 (t, C-2), 23.2 (q, C-2'), 23.7 (t, C-6), 23.7 (q, C-29), 25.3 (q, C-28), 27.0 (q, C-24), 28.6 (t, C-11), 28.9 (t, C-21), 31.2 (t, C-12), 31.7 (d, C-13), 31.7 (C-17, s), 32.1 (t, C-16), 34.7 (s, C-10), 35.0 (d, C-19), 35.9 (s, C-4), 37.4 (t, C-1), 37.4 (t, C-22), 37.6 (d, C-20), 40.9 (s, C-14), 47.7 (d, C-18), 50.2 (d, C-5), 54.5 (d, C-9), 80.4 (d, C-3), 116.2 (d, C-7), 144.9 (s, C-8), 169.0 (s, C-1'). 分析以上波谱数据, 与文献(贾靓等, 2005)数据基本一致, 因此鉴定化合物 7 为降香萜醇乙酸酯。

**化合物 8** 白色固体 (CDCl<sub>3</sub>), mp = 79 ~ 80 °C, IR<sub>vmax</sub> (KBr) cm<sup>-1</sup>: 2 926, 2 855, 1 735, 1 665, 1 375, 1 346, 1 005, 970. 分子式为 C<sub>46</sub>H<sub>78</sub>O<sub>3</sub>, ESI-MS m/z: 679[M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.85 (3H, s, CH<sub>3</sub>), 0.89 (12H, s, CH<sub>3</sub> × 4), 1.12 (3H, s, CH<sub>3</sub>), 1.15 (3H, s, CH<sub>3</sub>), 1.35 (3H, s, CH<sub>3</sub>) 4.50 (1H, dd, J = 11.4, 4.8 Hz, H-3), 5.57 (1H, s, H-12); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 14.1 (q, C-16'), 16.1 (q, C-24), 16.4 (q, C-25), 17.4 (t, C-6), 18.7 (q, C-26), 22.8 (t, C-15'), 23.3 (q, C-27), 23.5 (q, C-30), 23.6 (t, C-2), 25.1 (t, C-3'), 26.4 (t, C-

15), 26.4 (t, C-16), 28.0 (q, C-23), 28.7 (q, C-28), 29.3-29.9 (t, C-4'-13'), 31.0 (s, C-20), 31.9 (t, C-14'), 32.3 (s, C-17), 32.7 (t, C-7), 33.0 (q, C-29), 34.2 (t, C-2'), 34.8 (t, C-21), 36.5 (t, C-22), 36.9 (s, C-10), 38.1 (s, C-4), 38.8 (t, C-1), 43.4 (d, C-8), 45.1 (t, C-19), 45.4 (s, C-14), 47.6 (d, C-18), 55.0 (d, C-5), 61.7 (d, C-9), 80.3 (d, C-3), 128.1 (d, C-12), 130.4 (s, C-13), 174.6 (s, C-1'), 200.1 (s, C-11)。分析以上波谱数据, 与文献(Menzeth *et al.*, 2002)数据基本一致, 因此鉴定化合物 8 为齐墩果烷-11-羰基-12-烯-3-醇棕榈酸酯。

**化合物 9** 白色无定形粉末 (CDCl<sub>3</sub>), mp = 178 ~ 179 °C, IR<sub>vmax</sub> (KBr) cm<sup>-1</sup>: 3 422, 3 050, 2 920, 1 660, 1 370, 1 343, 1 020, 970. 分子式为 C<sub>30</sub>H<sub>48</sub>O<sub>2</sub>, ESI-MS m/z: 441 [M]<sup>+</sup>, <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz) δ: 0.84, 0.86, 0.88, 0.98, 1.01, 1.68 (各 3H, CH<sub>3</sub> × 6), 3.34, 3.85 (各 1H, d, J = 10.4 Hz, H-28), 3.94 (1H, t, J = 2.6 Hz, H-3), 5.26 (1H, t, J = 5.3 Hz, H-12), 5.73 (2H, s, H-29); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 14.5 (q, C-27), 15.3 (q, C-24), 15.6 (q, C-26), 15.7 (q, C-25), 18.3 (t, C-6), 23.3 (t, C-11), 26.6 (t, C-15), 27.4 (t, C-2), 27.4 (q, C-30), 28.7 (q, C-23), 29.8 (t, C-21), 29.9 (t, C-16), 34.3 (t, C-22), 35.7 (t, C-7), 36.9 (s, C-10), 38.7 (t, C-1), 38.8 (s, C-4), 40.8 (s, C-8), 47.2 (s, C-17), 47.7 (d, C-18), 48.3 (d, C-19), 50.4 (d, C-9), 51.2 (s, C-14), 55.2 (d, C-5), 59.1 (t, C-28), 79.0 (d, C-3), 109.3 (t, C-29), 129.7 (d, C-12), 139.6 (s, C-13), 150.9 (s, C-20)。分析以上波谱数据, 与文献(Rasa *et al.*, 2002)数据基本一致, 因此鉴定化合物 9 为 12-烯基白桦脂醇。

**化合物 10** 白色粉末 (CDCl<sub>3</sub>), mp = 231 ~ 232 °C, IR<sub>vmax</sub> (KBr) cm<sup>-1</sup>: 3 420, 3 050, 1 660, 1 370, 1 342, 1 003, 965. 分子式为 C<sub>30</sub>H<sub>50</sub>O, ESI-MS m/z: 427[M]<sup>+</sup>, <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 0.85 (3H, d, J = 6.5 Hz, H-30), 0.89 (3H, d, J = 6.5 Hz, H-29), 0.78, 0.88, 0.92, 1.01, 1.04, 1.13 (各 3H, s, CH<sub>3</sub> × 6), 3.47 (1H, br s, H-3), 5.61 (1H, br s, H-6); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) δ: 14.5 (q, C-27), 15.2 (q, C-26), 15.5 (q, C-28), 17.3 (q, C-25), 17.6 (t, C-1), 19.4 (t, C-19), 21.9 (q, C-29), 22.9 (q, C-30), 23.5 (t, C-7), 24.9 (q, C-24), 27.3 (t, C-2), 27.8 (t, C-20), 28.5 (t, C-15), 28.5 (q, C-23), 28.6 (t, C-12), 30.3 (d,

C-22), 33.6(t, C-11), 34.3(s, C-9), 34.9(t, C-16), 38.1(s, C-13), 38.8(s, C-14), 40.3(s, C-4), 42.3(s, C-17), 43.7(d, C-8), 49.7(s, C-10), 51.2(d, C-18), 59.5(d, C-21), 75.8(d, C-3), 121.5(d, C-6), 141.5(s, C-5)。分析以上波谱数据, 与文献(温晶等, 2010)数据基本一致, 因此鉴定化合物 10 为西米杜鹃醇。

**化合物 11** 白色固体(CDCl<sub>3</sub>), mp = 56 ~ 57 °C, IR<sub>v<sub>max</sub></sub>(KBr) cm<sup>-1</sup>: 1 730, 1 668, 1 397, 1 366, 1 243, 1 023, 1 003, 984, 967. 分子式为 C<sub>30</sub>H<sub>88</sub>O<sub>2</sub>, ESI-MS m/z: 721 [M]<sup>+</sup>, <sup>1</sup>H-NMR(600 MHz, CDCl<sub>3</sub>) δ: 0.78(3H, s, H-28), 0.83(3H, s, H-25), 0.85(3H, s, H-24), 0.87(3H, s, H-23), 0.93(3H, s, H-27), 1.02(3H, s, H-26), 1.67(3H, s, H-30), 4.46(1H, dd, J = 10.9, 5.3 Hz, H-3), 4.56(1H, br s, H-29b), 4.67(1H, br s, H-29a), <sup>13</sup>C-NMR(150 MHz, CDCl<sub>3</sub>) δ: 14.1(q, C-20'), 14.5(q, C-27), 16.0(q, C-26), 16.2(q, C-25), 16.6(q, C-24), 18.0(q, C-28), 18.2(t, C-6), 19.3(q, C-30), 21.0(t, C-11), 22.8(t, C-19'), 23.7(t, C-2), 25.2(t, C-12), 25.2(t, C-3'), 27.4(t, C-15), 28.0(q, C-23), 29.2-29.9(t, C-4'-13'), 29.7(t, C-21), 31.9(t, C-18'), 34.2(t, C-7), 34.8(t, C-2'), 35.6(t, C-16), 37.1(s, C-10), 37.8(s, C-4), 38.1(d, C-13), 38.4(t, C-1), 40.0(s, C-22), 40.9(s, C-8), 42.8(s, C-14), 43.0(s, C-17), 48.0(d, C-19), 48.3(d, C-18), 50.4(d, C-9), 55.4(d, C-5), 80.6(d, C-3), 109.3(t, C-29), 150.9(s, C-20), 173.6(s, C-1')。分析以上波谱数据, 与文献(Hideyuki *et al.*, 2001)数据基本一致, 因此鉴定化合物 11 为二十烷酸羽扇豆醇乙酸酯。

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