

## 秦岭冷杉茎叶的化学成分研究

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**摘要:** 目的 研究秦岭冷杉 *Abies chensiensis* 茎叶的化学成分。方法 利用大孔吸附树脂、葡聚糖凝胶、硅胶柱色谱、半制备高效液相色谱等多种色谱方法分离纯化, 根据理化性质及波谱数据对化合物进行结构鉴定。结果 从秦岭冷杉 95%乙醇提取物中分离得到 24 个化合物, 分别鉴定为 7,14,24-mariesatrien-26,23-olide-3 $\alpha$ ,23-diol (1)、(23*R*)-3 $\alpha$ -hydroxy-9,19-cyclo-9 $\beta$ -lanost-24-en-26,23-olide (2)、7-oxocallitric acid (3)、23-hydroxy-3-oxomariesia-8 (9),14,24-trien-26,23-olide (4)、紫果冷杉三萜 E (5)、3-oxo-9 $\beta$ -lanosta-7,24-dien-26,23*R*-olide (6)、7,14,22*Z*,24-mariesatetraen-26,23-olide-3-one (7)、(+)-rel-3 $\alpha$ -hydroxy-23-oxocycloart-25 (27)-en-26-oic acid (8)、cycloart-25-en-3 $\beta$ ,24-diol (9)、紫果冷杉三萜 H (10)、3-oxo-24,25,26,27-tetranolanost-8-en-23-oic acid (11)、abiesadine C (12)、13 $\beta$ -epidioxy-8(14)-abieten-18-oic acid (13)、dehydroabietic acid (14)、15-hydroxydehydroabietic acid (15)、methyl 18-methoxydehydroabietate (16)、7 $\beta$ -hydroxy dehydroabietic acid (17)、dehydroabietan-18-ol (18)、centdaroic acid (19)、abietic acid (20)、6,8,11,13-abi-etatrien-18-oic acid (21)、abiesadine B (22)、abiesadine N (23)、12 $\beta$ -hydroxyabietic acid (24)。结论 所有化合物均为首次从该植物中分离得到, 其中化合物 11 为属内首次分离得到。

**关键词:** 秦岭冷杉; 三萜类化合物; 二萜类化合物; 紫果冷杉三萜 E; 紫果冷杉三萜 H

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## Study on chemical constituents of *Abies chensiensis*

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**Abstract: Objective** To study the chemical constituents of the stems and leaves parts of *Abies chensiensis*. **Methods** The isolation and purification were carried out by HP-20 macroporous resin, Sephadex LH-20, silica gel column chromatography, semi-preparative HPLC. Their structures were elucidated on the basis of physicochemical properties and spectroscopic data. **Results** Twenty-four compounds were isolated and elucidated from the stems and leaves parts of *A. chensiensis*, their structures were identified as 7,14,24-mariesatrien-26,23-olide-3 $\alpha$ ,23-diol (1), (23*R*)-3 $\alpha$ -hydroxy-9,19-cyclo-9 $\beta$ -lanost-24-en-26,23-olide (2), 7-oxocallitric acid (3), 23-hydroxy-3-oxomariesia-8 (9),14,24-trien-26,23-olide (4), neoabietrine E (5), 3-oxo-9 $\beta$ -lanosta-7,24-dien-26,23*R*-olide (6), 7,14,22*Z*,24-mariesatetraen-26,23-olide-3-one (7), (+)-rel-3 $\alpha$ -hydroxy-23-oxocycloart-25 (27)-en-26-oic acid (8), cycloart-25-en-3 $\beta$ ,24-diol (9), neoabietrine H (10), 3-oxo-24,25,26,27-tetranolanost-8-en-23-oic acid (11), abiesadine C (12), 13 $\beta$ -epidioxy-8(14)-abieten-18-oic acid (13), dehydroabietic acid (14), 15-hydroxydehydroabietic acid (15), methyl 18-methoxydehydroabietate (16), 7 $\beta$ -hydroxy dehydroabietic acid (17), dehydroabietan-18-ol (18), centdaroic acid (19), abietic acid (20), 6,8,11,13-abi-etatrien-18-oic acid (21), abiesadine B (22), abiesadine N (23), 12 $\beta$ -hydroxyabietic acid (24). **Conclusion** All compounds are isolated from the plants of *A. chensiensis* for the first time, and compound 11 is isolated from the *Abies* genus for the first time.

**Key words:** *Abies chensiensis* Tiegh.; triperpenoids; diterpenoids; neoabietrine E; neoabietrine H

秦岭冷杉 *Abies chensiensis* Tiegh. 是松科冷杉属一种高大的常绿乔木, 主要分布于陕西、河南、湖北以及甘肃等地。秦岭冷杉主要以球果入药, 具有调经、止血、消炎、止痛的功效。目前从该植物

中分离得到的化合物主要为羊毛甾烷型三萜类、松香烷型二萜类、黄酮以及木脂素类成分。本实验对秦岭冷杉的化学成分进行了系统研究, 从其茎叶 95%乙醇提取物中共分离鉴定了 24 个化合物, 分别

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为 mariesatrien-26,23-olide-3 $\alpha$ ,23-diol (**1**)、(23*R*)-3 $\alpha$ -hydroxy-9,19-cyclo-9 $\beta$ -lanost-24-en-26,23-olide (**2**)、7,14,24-7-oxocallitric acid (**3**)、23-hydroxy-3-oxomariesia-8(9),14,24-trien-26,23-olide (**4**)、紫果冷杉三萜 E(neoabiestrine E, **5**)、3-oxo-9 $\beta$ -lanosta-7,24-dien-26,23*R*-olide (**6**)、7,14,22*Z*,24-mariesatetraen-26,23-olide-3-one (**7**)、(+)-rel-3 $\alpha$ -hydroxy-23-oxocycloart-25(27)-en-26-oic acid (**8**)、cycloart-25-en-3 $\beta$ ,24-diol (**9**)、紫果冷杉三萜 H(neoabiestrine H, **10**)、3-oxo-24,25,26,27-tetranolanost-8-en-23-oic acid (**11**)、abiesadine C (**12**)、13 $\beta$ -epidioxy-8(14)-abieten-18-oic acid (**13**)、dehydroabietic acid (**14**)、15-hydroxydehydroabietic acid (**15**)、methyl 18-methoxydehydroabietate (**16**)、7 $\beta$ -hydroxy dehydroabietic acid (**17**)、dehydroabietan-18-ol (**18**)、centdaric acid (**19**)、abietic acid (**20**)、6,8,11,13-abi-etatrien-18-oic acid (**21**)、abiesadine B (**22**)、abiesadine N (**23**)、12 $\beta$ -hydroxyabietic acid (**24**)。所有化合物均为首次从该植物中分离得到,其中化合物 **11** 为首次该属中分离得到的化合物。

### 1 仪器与材料

Bruker ADVANCEIII 400 MHz 核磁共振波谱仪(美国 Bruker 公司); GCMS-TQ8030 质谱仪(日本岛津公司); 薄层色谱(TLC)硅胶(GF<sub>254</sub>, 10~40  $\mu$ m)、正相柱色谱硅胶(200~300 目), 青岛海洋化工厂; Waters 1525 半制备型高效液相色谱仪(美国 Waters 公司); 色谱柱: SunFire (C<sub>18</sub>, 150 mm $\times$ 4.6 mm, 5  $\mu$ m); 葡聚糖凝胶 LH-20 (Amersham Biosciences 公司); 大孔树脂 HP-20 (日本三菱公司); Laborota 4000 旋转蒸发仪(德国 Heidolph 公司); 色谱纯甲醇及其他分析纯试剂均来自于天津津南化工二厂。

秦岭冷杉枝叶于 2010 年 8 月采自陕西省宝鸡秦岭山, 并由兰州大学生命科学院张国梁教授鉴定为秦岭冷杉 *Abies chensiensis* Tiegh. 植物标本(20100824-02)存放于兰州大学重点实验室天然有机研究室。

### 2 提取与分离

干燥的秦岭冷杉枝叶 7.5 kg 粉碎后用 95% 的乙醇水(40 L)室温下浸泡 3 次, 每次 3 d。合并滤液减压浓缩得粗浸膏(700 g)。浸膏用水分散后用醋酸乙酯萃取 3 次, 得到醋酸乙酯部分浸膏(122 g)。该浸膏用少量的甲醇溶解后过大孔树脂柱色谱, 乙醇-水(3:7、5:5、8:2、10:0)梯度洗脱, 得

到 4 个组分(Fr. A~D)。

大孔树脂 80% 乙醇水洗脱部分减压蒸馏得粗样品 Fr. C。将该样品用少量的甲醇溶解后进行 MCI 柱色谱分离, 乙醇-水(3:7、5:5、8:2、10:0)梯度洗脱, 得到 4 个组分 Fr. C<sub>1</sub>~C<sub>4</sub>。

Fr. C<sub>2</sub> (2.0 g) 部分有大量白色固体析出, 用醋酸乙酯洗涤并且重结晶得到化合物 **11** (12 mg), 将除去此化合物后的剩余部分与 Fr. C<sub>1</sub> 和 Fr. C<sub>3</sub> 分别进行硅胶柱色谱(氯仿-醋酸乙酯 1:0 $\rightarrow$ 0:1)、葡聚糖凝胶柱色谱(纯甲醇)分离, 得化合物 **1** (1.2 mg)、**2** (2.1 mg)、**3** (3.0 mg)、**4** (4.0 mg)、**5** (3.8 mg)。制备 HPLC (甲醇-水 35:65) 分离得到化合物 **6** (6.2 mg,  $t_R$ =12.7 min)、**7** (4.9 mg,  $t_R$ =15.7 min)、**8** (5.2 mg,  $t_R$ =27.5 min)、**9** (2.7 mg,  $t_R$ =29.6 min)、**10** (3.2 mg,  $t_R$ =32.5 min)。

大孔树脂洗脱下来的 50% 部分(Fr. B) 共计 55 g, 该部分经硅胶柱色谱分离, 用石油醚-丙酮(1:0 $\rightarrow$ 0:1)为洗脱剂进行洗脱得到 5 个组分(Fr. B<sub>1</sub>~B<sub>5</sub>)。然后将 Fr. B<sub>1</sub>~B<sub>5</sub> 依次进行进一步的分离纯化, 分别进行反相硅胶柱色谱(甲醇-水 1:0 $\rightarrow$ 0:1)、葡聚糖凝胶色谱(纯甲醇)分离得到化合物 **12** (2.6 mg)、**13** (2.0 mg)、**14** (3.1 mg)、**15** (1.9 mg)、**16** (2.2 mg)、**17** (2.3 mg)、**18** (1.7 mg)。制备 HPLC (甲醇-水 30:70) 色谱进行纯化, 得到化合物 **19** (2.4 mg,  $t_R$ =10.6 min)、**20** (1.1 mg,  $t_R$ =12.7 min)、**21** (5.2 mg,  $t_R$ =15.5 min)、**22** (4.1 mg,  $t_R$ =22.7 min)、**23** (2.9 mg,  $t_R$ =27.6 min)、**24** (6.7 mg,  $t_R$ =31.5 min)。

### 3 结构鉴定

化合物 **1**: 为白色无定形粉末, EI-MS  $m/z$ : 468 [M]<sup>+</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.01, 0.95 (各 1H, m, H-1), 1.96, 1.61 (各 1H, m, H-2), 3.46 (1H, brs, H-3), 1.56 (1H, dd,  $J$ =11.4, 4.2 Hz, H-5), 1.86, 1.91 (各 1H, m, H-6), 5.56 (1H, d,  $J$ =5.1 Hz, H-7), 1.41 (1H, m, H-10), 1.82, 1.40 (各 1H, m, H-11), 1.84, 1.45 (各 1H, m, H-12), 5.18 (1H, brs, H-15), 2.18, 1.92 (2H, m, H-16), 0.89 (3H, s, 18-Me), 0.96 (3H, s, 19-Me), 2.03 (1H, m, H-20), 0.95 (3H, d,  $J$ =6.6 Hz, H-21), 1.68, 2.10 (各 1H, m, H-22), 6.88 (1H, brs, H-24), 1.91 (3H, s, 27-Me), 0.97 (3H, s, 28-Me), 0.95 (3H, s, 29-Me), 0.86 (3H, s, 30-Me); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 28.8 (C-1), 25.6 (C-2), 76.7 (C-3), 37.5 (C-4), 38.2 (C-5), 23.4 (C-6), 120.8 (C-7), 136.7 (C-8), 53.0

(C-9), 34.5 (C-10), 25.6 (C-11), 33.6 (C-12), 51.6 (C-13), 152.8 (C-14), 114.5 (C-15), 45.1 (C-16), 51.6 (C-17), 16.8 (C-18), 22.6 (C-19), 33.7 (C-20), 17.2 (C-21), 41.5 (C-22), 106.1 (C-23), 148.2 (C-24), 131.8 (C-25), 171.6 (C-26), 10.6 (C-27), 28.2 (C-28), 23.5 (C-29), 19.2 (C-30)。以上波谱数据与文献报道一致<sup>[1]</sup>, 故鉴定化合物 **1** 为 7,14,24-mariesatrien-26,23-olide-3 $\alpha$ ,23-diol。

化合物 **2**: 白色无定形粉末, EI-MS  $m/z$ : 468  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.45 (1H, brs, H-3), 0.89 (3H, s, 18-Me), 0.35, 0.51 (各 1H, d,  $J = 4.2$  Hz, H-19), 0.98 (3H, d,  $J = 7.2$  Hz, 21-Me), 4.99 (1H, m, H-23), 6.96 (1H, s, H-24), 1.91 (1H, s, 27-Me), 0.95 (3H, s, 28-Me), 0.86 (3H, s, 29-Me), 0.86 (3H, s, Me-30);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 28.6 (C-1), 27.7 (C-2), 77.1 (C-3), 40.0 (C-4), 41.0 (C-5), 21.1 (C-6), 25.7 (C-7), 48.1 (C-8), 19.8 (C-9), 26.6 (C-10), 26.5 (C-11), 33.2 (C-12), 45.6 (C-13), 49.2 (C-14), 35.6 (C-15), 28.5 (C-16), 52.8 (C-17), 18.2 (C-18), 29.7 (C-19), 33.6 (C-20), 18.2 (C-21), 40.7 (C-22), 79.2 (C-23), 149.5 (C-24), 129.2 (C-25), 174.6 (C-26), 10.5 (C-27), 25.6 (C-28), 21.2 (C-29), 19.6 (C-30)。以上波谱数据与文献报道一致<sup>[2]</sup>, 故鉴定化合物 **2** 为 (23*R*)-3 $\alpha$ -hydroxy-9,19-cyclo-9 $\beta$ -lanost-24-en-26,23-olide。

化合物 **3**: 无色油状物; EI-MS  $m/z$ : 314  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.26 (3H, s, 20-Me), 1.24 (3H, d,  $J = 6.8$  Hz, 16-Me), 1.26 (3H, d,  $J = 6.8$  Hz, 17-Me), 1.34 (3H, s, 19-Me), 7.86 (1H, d,  $J = 2.2$  Hz, H-14), 7.40 (1H, dd,  $J = 2.2, 8.0$  Hz, H-12), 7.30 (1H, d,  $J = 8.0$  Hz, H-11);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 37.9 (C-1), 18.3 (C-2), 36.8 (C-3), 46.6 (C-4), 43.7 (C-5), 36.9 (C-6), 198.2 (C-7), 130.3 (C-8), 153.4 (C-9), 36.8 (C-10), 124.8 (C-11), 123.7 (C-12), 146.7 (C-13), 132.7 (C-14), 33.8 (C-15), 23.5 (C-16), 23.7 (C-17), 183.7 (C-18), 16.3 (C-19), 25.2 (C-20)。以上波谱数据与文献报道一致<sup>[3]</sup>, 故鉴定化合物 **3** 为 7-oxocallitrisic acid。

化合物 **4**: 白色无定形粉末, EI-MS  $m/z$ : 466  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.60, 1.91 (各 1H, m, H-1), 2.58, 2.45 (各 1H, m, H-2), 1.66 (1H, m, H-5), 1.99~2.21 (2H, m, H-6), 1.61~1.72 (2H, m, H-7), 1.70, 2.46 (各 1H, m, H-11), 1.52~1.81 (2H, m,

H-12), 5.36 (1H, brs, H-15), 1.95, 2.31 (各 1H, m, H-16), 0.78 (3H, s, 18-Me), 1.14 (3H, s, 19-Me), 1.12 (1H, m, H-20), 1.00 (3H, d,  $J = 7.0$  Hz, 21-Me), 2.17 (2H, m, H-22), 6.89 (1H, m, H-24), 1.92 (3H, s, 27-Me), 1.13 (3H, s, 28-Me), 1.08 (3H, s, 29-Me), 0.89 (3H, s, 30-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 34.5 (C-1), 33.2 (C-2), 217.6 (C-3), 47.2 (C-4), 51.3 (C-5), 22.7 (C-6), 19.6 (C-7), 123.8 (C-8), 140.1 (C-9), 37.9 (C-10), 34.5 (C-11), 30.2 (C-12), 47.9 (C-13), 148.1 (C-14), 116.6 (C-15), 44.8 (C-16), 50.1 (C-17), 17.5 (C-18), 18.6 (C-19), 33.5 (C-20), 17.1 (C-21), 41.0 (C-22), 106.6 (C-23), 147.5 (C-24), 131.6 (C-25), 171.6 (C-26), 10.4 (C-27), 26.8 (C-28), 21.6 (C-29), 15.7 (C-30)。以上波谱数据与文献报道一致<sup>[4]</sup>, 故鉴定化合物 **4** 为 23-hydroxy-3-oxomariesia-8(9), 14,24-trien-26,23-olide。

化合物 **5**: 白色无定形粉末, EI-MS  $m/z$ : 482  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.66, 1.89 (各 1H, m, H-1), 2.52, 2.47 (各 1H, m, H-2), 1.62 (1H, m, H-5), 1.56, 1.66 (各 1H, m, H-6), 2.01, 2.15 (各 1H, m, H-7), 1.96 (2H, m, H-11), 1.41, 1.96 (各 1H, m, H-12), 2.37 (2H, m, H-15), 1.55, 1.46 (各 1H, m, H-16), 0.86 (3H, s, 18-Me), 1.02 (3H, s, 19-Me), 2.37 (1H, m, H-20), 0.82 (3H, d,  $J = 6.4$  Hz, H-21), 2.20, 2.67 (各 1H, m, H-22), 2.41, 2.77 (1H, m, H-24), 2.96 (1H, m, H-25), 1.14 (3H, d,  $J = 6.8$  Hz, 27-Me), 1.11 (3H, s, 28-Me), 1.08 (3H, s, 29-Me), 4.56, 4.77 (各 1H, s, H-30), 3.67 (3H, s, OMe);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 35.5 (C-1), 34.5 (C-2), 217.6 (C-3), 47.4 (C-4), 51.1 (C-5), 20.2 (C-6), 26.6 (C-7), 136.2 (C-8), 147.8 (C-9), 35.6 (C-10), 26.7 (C-11), 32.4 (C-12), 68.2 (C-13), 155.1 (C-14), 27.2 (C-15), 37.7 (C-16), 49.1 (C-17), 18.6 (C-18), 18.6 (C-19), 34.2 (C-20), 16.3 (C-21), 45.3 (C-22), 208.6 (C-23), 46.5 (C-24), 34.7 (C-25), 176.5 (C-26), 17.2 (C-27), 26.6 (C-28), 21.2 (C-29), 103.7 (C-30), OMe (51.7)。以上波谱数据与文献报道一致<sup>[5]</sup>, 故鉴定化合物 **5** 为紫果冷杉三萜 E。

化合物 **6**: 白色无定形粉末, EI-MS  $m/z$ : 452  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.67 (1H, dt,  $J = 6.5, 3.1$  Hz, H-7), 4.96 (1H, m, H-23), 7.01 (1H, s, H-24), 1.92 (3H, s, Me-27), 0.82 (3H, s, Me-18), 1.01 (3H, s, Me-19), 1.02 (3H, d,  $J = 6.6$  Hz, Me-21), 1.11

(3H, s, Me-28), 1.10 (3H, s, Me-29), 1.05 (3H, s, Me-30);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 34.2 (C-1), 34.5 (C-2), 218.6 (C-3), 47.2 (C-4), 52.5 (C-5), 23.2 (C-6), 121.6 (C-7), 148.6 (C-8), 45.9 (C-9), 35.8 (C-10), 21.1 (C-11), 34.6 (C-12), 44.2 (C-13), 51.8 (C-14), 33.2 (C-15), 28.6 (C-16), 53.6 (C-17), 22.3 (C-18), 23.2 (C-19), 33.6 (C-20), 18.2 (C-21), 40.2 (C-22), 79.2 (C-23), 149.6 (C-24), 129.5 (C-25), 174.2 (C-26), 10.6 (C-27), 21.3 (C-28), 28.3 (C-29), 27.6 (C-30)。以上波谱数据与文献报道一致<sup>[6]</sup>, 故鉴定化合物 **6** 为 3-oxo-9 $\beta$ -lanosta-7,24-dien-26,23R-olide。

化合物 **7**: 白色无定形粉末, EI-MS  $m/z$ : 448  $[\text{M}]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.81, 1.52 (各 1H, m, H-1), 2.25, 2.73 (各 1H, m, H-2), 1.52 (1H, m, H-5), 2.01 (2H, m, H-6), 5.66 (1H, brs, H-7), 1.51 (1H, m, H-9), 1.52, 1.70 (各 1H, m, H-11), 1.26, 1.70 (各 1H, m, H-12), 5.26 (1H, brs, H-15), 2.27, 2.02 (2H, m, H-16), 1.01 (3H, s, 18-Me), 1.11 (3H, s, 19-Me), 3.27 (1H, m, H-20), 1.03 (3H, d,  $J = 7.2$  Hz, H-21), 5.17 (1H, d,  $J = 10.6$  Hz, H-22), 6.96 (1H, brs, H-24), 1.97 (3H, s, 27-Me), 1.07 (3H, s, 28-Me), 1.15 (3H, s, 29-Me), 0.81 (3H, s, 30-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 35.7 (C-1), 35.3 (C-2), 216.7 (C-3), 47.3 (C-4), 44.6 (C-5), 23.6 (C-6), 120.5 (C-7), 136.5 (C-8), 52.7 (C-9), 34.7 (C-10), 24.5 (C-11), 31.5 (C-12), 51.7 (C-13), 152.0 (C-14), 115.2 (C-15), 44.8 (C-16), 50.6 (C-17), 17.1 (C-18), 22.6 (C-19), 36.7 (C-20), 17.6 (C-21), 118.2 (C-22), 146.7 (C-23), 138.2 (C-24), 128.7 (C-25), 171.2 (C-26), 10.7 (C-27), 25.6 (C-28), 21.2 (C-29), 19.2 (C-30)。以上波谱数据与文献报道一致<sup>[7]</sup>, 故鉴定化合物 **7** 为 7,14,22Z,24-mariesatetraen-26,23-olide-3-one。

化合物 **8**: 白色无定形粉末, EI-MS  $m/z$ : 470  $[\text{M}]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.01, 1.82 (各 1H, m, H-1), 1.62, 1.96 (各 1H, m, H-2), 3.46 (1H, brs, H-3), 1.86 (1H, m, H-5), 1.45, 0.78 (各 1H, m, H-6), 1.13, 1.31 (各 1H, m, H-7), 1.56 (1H, m, H-8), 2.01, 1.15 (各 1H, m, H-11), 1.62 (2H, m, H-12), 1.31 (2H, m, H-15), 1.87, 1.27 (各 1H, m, H-16), 1.62 (1H, m, H-17), 1.01 (3H, s, 18-Me), 0.37, 0.52 (各 1H, d,  $J = 4.0$  Hz, H-19), 2.06 (1H, m, H-20), 0.87 (3H, d,  $J = 7.2$  Hz, 21-Me), 2.26, 2.59 (各 1H, m, H-22), 3.41, 3.36 (各 1H, d,  $J = 16.8$  Hz, H-24), 6.46, 5.73 (1H,

brs, H-27), 0.95 (3H, s, 28-Me), 0.87 (3H, s, 29-Me), 0.92 (3H, s, 30-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 27.7 (C-1), 28.5 (C-2), 77.2 (C-3), 39.8 (C-4), 41.2 (C-5), 21.1 (C-6), 25.9 (C-7), 48.2 (C-8), 19.7 (C-9), 26.6 (C-10), 26.6 (C-11), 32.8 (C-12), 45.0 (C-13), 49.2 (C-14), 35.2 (C-15), 28.5 (C-16), 52.6 (C-17), 18.2 (C-18), 29.6 (C-19), 32.8 (C-20), 19.4 (C-21), 50.1 (C-22), 207.6 (C-23), 46.5 (C-24), 133.7 (C-25), 170.6 (C-26), 130.5 (C-27), 25.5 (C-28), 21.2 (C-29), 19.3 (C-30)。以上波谱数据与文献报道一致<sup>[8]</sup>, 故鉴定化合物 **8** 为 (+)-rel-3 $\alpha$ -hydroxy-23-oxocycloart-25(27)-en-26-oic acid。

化合物 **9**: 白色无定形粉末, EI-MS  $m/z$ : 442  $[\text{M}]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.86, 4.92 (各 1H, brs, H-26), 4.02 (1H, t,  $J = 6.8$  Hz, H-24), 3.27 (1H, dd,  $J = 4.6, 11.2$  Hz, H-3), 1.72 (3H, s, 27-Me), 0.96, 0.96 (各 3H, s, 18, 30-Me), 0.88 (3H, d,  $J = 6.4$  Hz, 21-Me), 0.78 (3H, s, 29-Me), 0.33, 0.57 (各 1H, d,  $J = 4.4$  Hz, H-19);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 32.2 (C-1), 30.5 (C-2), 79.1 (C-3), 40.7 (C-4), 47.0 (C-5), 21.6 (C-6), 28.5 (C-7), 48.5 (C-8), 20.2 (C-9), 26.6 (C-10), 26.5 (C-11), 33.1 (C-12), 45.7 (C-13), 49.1 (C-14), 35.7 (C-15), 26.5 (C-16), 52.7 (C-17), 17.8 (C-18), 29.7 (C-19), 36.2 (C-20), 18.6 (C-21), 32.1 (C-22), 29.2 (C-23), 76.5 (C-24), 147.7 (C-25), 111.2 (C-26), 17.7 (C-27), 19.2 (C-28), 14.2 (C-29), 25.6 (C-30)。以上波谱数据与文献报道一致<sup>[9]</sup>, 故鉴定化合物 **9** 为 cycloart-25-en-3 $\beta$ ,24-diol。

化合物 **10**: 白色无定形粉末, EI-MS:  $m/z$  476  $[\text{M}]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.06, 1.87 (各 1H, m, H-1), 1.82, 1.56 (各 1H, m, H-2), 3.76 (1H, brs, H-3), 2.22 (1H, m, H-5), 1.51, 0.81 (各 1H, m, H-6), 1.31, 1.17 (各 1H, m, H-7), 1.58 (H, m, H-8), 1.18, 2.06 (各 1H, m, H-11), 1.68 (2H, m, H-12), 1.32 (2H, m, H-15), 1.93, 1.77 (各 1H, m, H-16), 1.66 (1H, m, H-17), 1.02 (3H, s, 18-Me), 0.37, 0.55 (各 1H, d,  $J = 4.4$  Hz, H-19), 1.44 (1H, m, H-20), 0.92 (3H, d,  $J = 6.6$  Hz, 21-Me), 1.81, 0.97 (各 1H, m, H-22), 1.07, 1.32 (各 1H, m, H-23), 3.16 (1H, dd,  $J = 1.2, 10.0$  Hz H-24), 1.15 (3H, s, 26-Me), 1.16 (3H, s, 27-Me), 3.40, 3.56 (各 1H, d,  $J = 10.8$  Hz, 28-Me), 0.77 (3H, s, 29-Me), 0.99 (3H, s, 30-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 28.7 (C-1), 30.2 (C-2), 77.6 (C-3), 43.8

(C-4), 37.7 (C-5), 22.2 (C-6), 26.7 (C-7), 49.2 (C-8), 21.2 (C-9), 27.1 (C-10), 27.5 (C-11), 34.2 (C-12), 46.0 (C-13), 50.1 (C-14), 36.8 (C-15), 29.3 (C-16), 53.5 (C-17), 18.8 (C-18), 30.6 (C-19), 37.7 (C-20), 19.1 (C-21), 35.1 (C-22), 29.6 (C-23), 80.6 (C-24), 73.7 (C-25), 24.8 (C-26), 25.7 (C-27), 70.6 (C-28), 17.2 (C-29), 19.8 (C-30)。以上波谱数据与文献报道一致<sup>[5]</sup>, 故鉴定化合物 **10** 为紫果冷杉三萜 H。

化合物 **11**: 白色无定形粉末, EI-MS  $m/z$ : 400  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.97, 1.62 (各 1H, m, H-1), 2.41, 2.57 (各 1H, m, H-2), 1.60 (1H, m, H-5), 2.05 (2H, m, H-6), 2.07 (2H, m, H-7), 0.77 (3H, s, 18-Me), 1.12 (3H, s, 19-Me), 1.01 (3H, d,  $J = 4.0$  Hz, 21-Me), 1.11 (3H, s, 28-Me), 1.06 (3H, s, 29-Me), 0.91 (3H, s, 30-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 36.1 (C-1), 34.5 (C-2), 217.7 (C-3), 47.5 (C-4), 51.2 (C-5), 21.2 (C-6), 26.2 (C-7), 133.1 (C-8), 135.2 (C-9), 36.7 (C-10), 30.7 (C-11), 30.6 (C-12), 44.5 (C-13), 50.2 (C-14), 19.3 (C-15), 121.3 (C-16), 156.6 (C-17), 20.7 (C-18), 18.6 (C-19), 28.1 (C-20), 23.2 (C-21), 28.1 (C-22), 178.3 (C-23), 26.1 (C-28), 21.2 (C-29), 24.2 (C-30)。以上波谱数据与文献报道一致<sup>[10]</sup>, 故鉴定化合物 **11** 为 3-oxo-24,25,26,27-tetranolanost-8-en-23-oic acid。

化合物 **12**: 白色无定形粉末; EI-MS  $m/z$ : 352  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.55, 0.86 (各 1H, m, H-1), 1.45, 1.37 (各 1H, m, H-2), 1.62, 1.45 (各 1H, m, H-3), 1.56 (1H, m, H-5), 1.56, 1.02 (1H, m, H-6), 1.97, 1.27 (1H, m, H-7), 1.05 (1H, m, H-9), 1.87 (1H, dd,  $J = 15.0, 6.0$  Hz, H-11), 1.80 (1H, dd,  $J = 15.0, 2.4$  Hz, H-11), 3.28 (1H, m, H-12), 3.11 (1H, s, H-14), 1.48 (1H, m, H-15), 0.90, 0.87 (各 3H, d,  $J = 6.9$  Hz, 16, 17-Me), 1.08, 0.96 (各 3H, s, 19, 20-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.7 (C-1), 17.2 (C-2), 36.5 (C-3), 46.7 (C-4), 49.1 (C-5), 19.8 (C-6), 34.5 (C-7), 71.9 (C-8), 41.6 (C-9), 35.6 (C-10), 20.7 (C-11), 62.7 (C-12), 65.3 (C-13), 71.1 (C-14), 34.1 (C-15), 17.0 (C-16), 17.2 (C-17), 181.6 (C-18), 16.7 (C-19), 15.5 (C-20)。以上波谱数据与文献报道一致<sup>[11]</sup>, 故鉴定化合物 **12** 为 abiesadine C。

化合物 **13**: 无色油状物; EI-MS  $m/z$ : 334  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.13 (3H, s, 20-Me), 0.97 (3H, d,  $J = 7.8$  Hz, 16-Me), 0.98 (3H, d,  $J = 7.8$

Hz, 17-Me), 1.32 (3H, s, 19-Me), 6.13 (1H, s, H-14);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 33.4 (C-1), 17.5 (C-2), 37.3 (C-3), 47.1 (C-4), 40.0 (C-5), 20.5 (C-6), 27.3 (C-7), 143.7 (C-8), 82.1 (C-9), 38.4 (C-10), 23.4 (C-11), 25.1 (C-12), 79.7 (C-13), 126.9 (C-14), 32.1 (C-15), 17.5 (C-16), 17.4 (C-17), 184.6 (C-18), 17.1 (C-19), 17.8 (C-20)。以上波谱数据与文献报道一致<sup>[12]</sup>, 故鉴定化合物 **13** 为 13 $\beta$ -epidioxy-8 (14)-abieten-18-oic acid。

化合物 **14**: 白色无定形粉末; EI-MS  $m/z$ : 300  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.17 (1H, d,  $J = 8.1$  Hz, H-11), 7.03 (1H, d,  $J = 8.1$  Hz, H-12), 6.87 (1H, brs, H-14), 2.83, (1H, m, H-15), 1.27, 1.24 (各 3H, s, 19, 20-Me), 1.23, 1.23 (各 3H, d,  $J = 6.7$  Hz, 16, 17-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.0 (C-1), 18.7 (C-2), 37.2 (C-3), 47.2 (C-4), 44.7 (C-5), 21.8 (C-6), 30.4 (C-7), 135.0 (C-8), 146.5 (C-9), 36.3 (C-10), 124.3 (C-11), 123.3 (C-12), 145.8 (C-13), 127.1 (C-14), 33.4 (C-15), 24.2 (C-16), 24.2 (C-17), 184.3 (C-18), 16.6 (C-19), 25.2 (C-20)。以上波谱数据与文献报道一致<sup>[13]</sup>, 故鉴定化合物 **14** 为 dehydroabietic acid。

化合物 **15**: 白色无定形粉末; EI-MS  $m/z$ : 316  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.17 (1H, brs, H-11), 7.17 (1H, brs, H-12), 7.09 (1H, s, H-14), 1.47, 1.47, 1.18, 1.22 (各 3H, s, H-16, 17, 19, 20);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 39.6 (C-1), 20.1 (C-2), 38.5 (C-3), 48.5 (C-4), 22.9 (C-5), 46.9 (C-6), 31.5 (C-7), 135.8 (C-8), 149.4 (C-9), 38.1 (C-10), 125.9 (C-11), 124.9 (C-12), 147.3 (C-13), 123.0 (C-14), 72.8 (C-15), 31.9 (C-16), 31.9 (C-17), 183.8 (C-18), 18.0 (C-19), 25.6 (C-20)。以上波谱数据与文献报道一致<sup>[11]</sup>, 故鉴定化合物 **15** 为 15-hydroxydehydroabietic acid。

化合物 **16**: 无色油状物; EI-MS  $m/z$ : 344  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.18 (1H, m, H-5), 2.86 (1H, m, H-7), 7.22, (1H, d,  $J = 8.4$  Hz, H-11), 7.17 (1H, d,  $J = 8.4$  Hz, H-12), 7.04 (1H, d,  $J = 2.2$  Hz, H-14), 1.50, 1.50 (各 3H, s, 16, 17-Me), 1.29, 1.22 (各 3H, s, 19, 20-Me), 3.07, 3.68 (各 3H, s, OMe);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 37.9 (C-1), 18.6 (C-2), 37.0 (C-3), 47.7 (C-4), 44.8 (C-5), 21.7 (C-6), 30.1 (C-7), 134.5 (C-8), 148.0 (C-9), 36.6 (C-10), 124.0 (C-11), 123.3 (C-12), 142.7 (C-13), 126.3

(C-14), 77.2 (C-15), 27.9 (C-16), 27.9 (C-17), 179.1 (C-18), 16.5 (C-19), 25.1 (C-20), 50.6 (OMe), 51.9 (OMe)。以上波谱数据与文献报道一致<sup>[14]</sup>, 故鉴定化合物 **16** 为 methyl 18-methoxydehydroabietate。

化合物 **17**: 白色无定形粉末; EI-MS  $m/z$ : 316  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.47 (1H, dd,  $J = 2.7, 12.9$  Hz, H-5), 2.88 (1H, m, H-15), 4.89 (1H, dd,  $J = 1.96, 7.45$  Hz, H-7), 7.09 (1H, brs, H-12), 7.20 (1H, brs, H-11), 7.36, (1H, brs, H-14), 1.15 (3H, s, 11-Me), 1.28, 1.28 (各 3H, d,  $J = 6.9$  Hz, 16, 17-Me), 1.54 (3H, s, 19-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 39.5 (C-1), 19.9 (C-2), 38.2 (C-3), 48.2 (C-4), 46.7 (C-5), 22.8 (C-6), 31.4 (C-7), 136.0 (C-8), 149.9 (C-9), 38.3 (C-10), 125.3 (C-11), 124.3 (C-12), 143.3 (C-13), 127.4 (C-14), 78.1 (C-15), 28.2 (C-16), 28.3 (C-17), 184.8 (C-18), 17.6 (C-19), 25.5 (C-20), 50.8 (OMe)。以上波谱数据与文献报道一致<sup>[15]</sup>, 故鉴定化合物 **17** 为 7 $\beta$ -hydroxy dehydroabietic acid。

化合物 **18**: 无色油状物; EI-MS  $m/z$ : 286  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.92 (3H, s, 19-Me), 1.24 (3H, s, 20-Me), 1.23 (3H, d,  $J = 7.0$  Hz, 16-Me), 1.23 (3H, d,  $J = 7.0$  Hz, 17-Me), 3.25, 3.49 (各 1H, d,  $J = 11.0, 11.0$  Hz, H-18), 6.92 (1H, d,  $J = 1.6$  Hz, H-14), 7.01 (1H, dd,  $J = 8.4, 1.6$  Hz, H-12), 7.19 (1H, d,  $J = 8.4$  Hz, H-11);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.5 (C-1), 18.9 (C-2), 35.2 (C-3), 37.7 (C-4), 44.2 (C-5), 18.8 (C-6), 30.4 (C-7), 135.0 (C-8), 147.2 (C-9), 37.3 (C-10), 123.7 (C-11), 124.3 (C-12), 145.3 (C-13), 126.4 (C-14), 33.5 (C-15), 24.2 (C-16), 24.2 (C-17), 72.5 (C-18), 17.6 (C-19), 25.3 (C-20)。以上波谱数据与文献报道一致<sup>[16]</sup>, 故鉴定化合物 **18** 为 dehydroabietan-18-ol。

化合物 **19**: 为白色无定形粉末; EI-MS  $m/z$ : 298  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.03 (1H, d,  $J = 8.0$  Hz, H-11), 6.92 (1H, d,  $J = 8.0$ , H-12), 6.80 (1H, s, H-14), 1.19, 1.19 (各 3H, d,  $J = 4.0$  Hz, 16, 17-Me), 1.16, 1.14 (各 3H, s, 19, 20-Me), 5.28 (1H, m, H-6), 2.90 (2H, m, H-7), 2.15 (2H, m, H-15);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.3 (C-1), 18.9 (C-2), 37.2 (C-3), 47.8 (C-4), 137.2 (C-5), 123.8 (C-6), 32.3 (C-7), 135.0 (C-8), 147.1 (C-9), 37.1 (C-10), 124.4 (C-11), 124.2 (C-12), 146.1 (C-13), 127.2 (C-14), 33.8 (C-15), 24.3 (C-16), 24.3 (C-17), 185.0 (C-18), 16.6 (C-19), 25.4

(C-20)。以上波谱数据与文献报道一致<sup>[17]</sup>, 故鉴定化合物 **19** 为 centdaric acid。

化合物 **20**: 无色油状物; EI-MS  $m/z$ : 302  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.01 (3H, d,  $J = 6.6$  Hz, 17-Me), 1.02 (3H, d,  $J = 6.6$  Hz, 16-Me), 1.26 (3H, s, 19-Me), 5.78 (1H, s, H-14), 5.38 (1H, t,  $J = 2.4$  Hz, H-7);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.3 (C-1), 18.0 (C-2), 37.2 (C-3), 46.3 (C-4), 44.9 (C-5), 25.6 (C-6), 120.5 (C-7), 135.6 (C-8), 50.9 (C-9), 34.5 (C-10), 22.5 (C-11), 27.4 (C-12), 145.3 (C-13), 122.4 (C-14), 34.9 (C-15), 20.9 (C-16), 21.4 (C-17), 184.9 (C-18), 16.7 (C-19), 14.0 (C-20)。以上波谱数据与文献报道一致<sup>[18]</sup>, 故鉴定化合物 **20** 为 abietic acid。

化合物 **21**: 无色油状物; EI-MS  $m/z$ : 298  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.17 (3H, s, 20-Me), 1.30, 1.30 (各 3H, d,  $J = 10.5$  Hz, 16, 17-Me), 1.47 (3H, s, 19-Me), 5.88 (1H, dd,  $J = 2.2, 8.2$  Hz, H-6), 5.61 (1H, dd,  $J = 2.2, 8.2$  Hz, H-7), 7.01 (1H, brs, H-14), 7.14 (1H, m, H-12), 7.17 (1H, m, H-11);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 35.8 (C-1), 18.4 (C-2), 35.2 (C-3), 46.2 (C-4), 46.4 (C-5), 129.8 (C-6), 125.7 (C-7), 132.6 (C-8), 146.5 (C-9), 38.4 (C-10), 124.6 (C-11), 121.7 (C-12), 145.1 (C-13), 128.5 (C-14), 33.7 (C-15), 24.2 (C-16), 24.1 (C-17), 184.1 (C-18), 17.7 (C-19), 20.9 (C-20)。以上波谱数据与文献报道一致<sup>[13]</sup>, 故鉴定化合物 **21** 为 6,8,11,13-abi-etatrien-18-oic acid。

化合物 **22**: 白色无定形粉末; EI-MS  $m/z$ : 334  $[M]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.79 (1H, d,  $J = 8.4$  Hz, H-11), 6.94 (1H, dd,  $J = 8.4, 1.8$  Hz, H-12), 6.91 (1H, d,  $J = 1.8$  Hz, H-14), 2.84 (1H, m, H-15), 2.53 (1H, m, H-5), 2.84, 2.68 (各 1H, m, H-7), 1.94, 1.81 (各 1H, m, H-1), 1.80, 1.68 (各 1H, m, H-2), 1.74, 1.56 (各 1H, m, H-3), 1.53 (1H, m, H-6), 1.22, 1.22 (各 3H, d,  $J = 7.2$  Hz, 16, 17-Me), 1.11, 1.01 (各 3H, s, 19, 20-Me);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 41.3 (C-1), 18.0 (C-2), 37.0 (C-3), 48.8 (C-4), 52.9 (C-5), 25.6 (C-6), 34.7 (C-7), 135.4 (C-8), 153.2 (C-9), 80.1 (C-10), 123.5 (C-11), 124.5 (C-12), 143.6 (C-13), 127.5 (C-14), 33.4 (C-15), 24.2 (C-16), 24.2 (C-17), 182.8 (C-18), 16.1 (C-19), 20.7 (C-20)。以上波谱数据与文献报道一致<sup>[11]</sup>, 故鉴定化合物 **22** 为 abiesadine B。

化合物 **23**: 无色油状物; EI-MS  $m/z$ : 332  $[M]^+$ ;

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.19, 1.90 (各 1H, m, H-1), 1.57 (2H, m, H-2), 1.64, 1.80 (各 1H, m, H-3), 2.10 (1H, m, H-5), 1.09, 2.15 (各 1H, m, H-6), 5.50, (1H, brs, H-7), 2.22 (1H, d,  $J = 13.7$  Hz, H-9), 1.88, 2.11 (各 1H, H-11), 3.83 (1H, t,  $J = 2.9$  Hz, H-12), 5.85 (1H, s, H-14), 2.31 (1H, m, H-15), 1.03, 1.06 (各 3H, d,  $J = 6.9$  Hz, 16, 17-Me), 1.23, 0.83 (各 3H, s, 19, 20-Me), 3.36 (3H, s, OMe);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 39.5 (C-1), 19.2 (C-2), 38.8 (C-3), 47.5 (C-4), 46.4 (C-5), 25.9 (C-6), 125.1 (C-7), 136.1 (C-8), 45.3 (C-9), 35.1 (C-10), 26.9 (C-11), 77.0 (C-12), 143.2 (C-13), 127.6 (C-14), 34.0 (C-15), 22.2 (C-16), 22.6 (C-17), 182.9 (C-18), 17.5 (C-19), 14.7 (C-20), 56.6 (OMe)。以上波谱数据与文献报道一致<sup>[19]</sup>, 故鉴定化合物 **23** 为 abiesadine N。

化合物 **24**: 无色油状物; EI-MS  $m/z$ : 318  $[\text{M}]^+$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.84 (3H, s, 20-Me), 1.07 (3H, d,  $J = 7.0$  Hz, 16-Me), 1.05 (3H, d,  $J = 7.0$  Hz, 17-Me), 1.26 (3H, s, 19-Me), 5.79 (1H, s, H-14), 4.44 (1H, dd,  $J = 3.5, 10.0$  Hz, H-12), 5.50 (1H, brs, H-7);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.1 (C-1), 17.9 (C-2), 37.1 (C-3), 46.1 (C-4), 44.1 (C-5), 25.6 (C-6), 122.3 (C-7), 134.7 (C-8), 48.4 (C-9), 34.4 (C-10), 33.1 (C-11), 69.5 (C-12), 147.1 (C-13), 123.4 (C-14), 28.0 (C-15), 20.6 (C-16), 22.7 (C-17), 184.4 (C-18), 16.7 (C-19), 14.1 (C-20)。以上波谱数据与文献报道一致<sup>[20]</sup>, 故鉴定化合物 **24** 为 12 $\beta$ - hydroxyabietic acid。

#### 参考文献

- [1] Hui Y G, Li J W, Takahisa N, *et al.* Rearranged lanostane triterpenoids from *Abies sachalinensis* (III) [J]. *Chem Pharm Bull*, 2008, 56(9): 1352-1354.
- [2] Barrero A F, Sanchez J F, Alvarez-Manzaneda E J, *et al.* Diterpenoids and cyclolanostanolides from *Abies marocana* [J]. *Phytochemistry*, 1992, 31(2): 615-620.
- [3] Carolina E M, Lozada M C, Hernández O S, *et al.*  $^1\text{H}$  and  $^{13}\text{C}$  NMR characterization of new cycloartane triterpenes from *Mangifera indica* [J]. *Mag Res Chem Mrc*, 2012, 50(1): 52-57.
- [4] Handa M, Murata T, Kobayashi K, *et al.* Lipase inhibitory and LDL anti-oxidative triterpenes from *Abies sibirica* [J]. *Phytochemistry*, 2013, 86(2): 168-175.
- [5] Li Y L, Gao Y X, Yang X W, *et al.* Cytotoxic triterpenoids from *Abies recurvata* [J]. *Phytochemistry*, 2012, 81(5): 159-164.
- [6] Tanaka R, Matsunaga S. 9 $\beta$ -lanostane-type triterpene lactones from the stem bark of *Abies veitchii* [J]. *J Nat Prod* [J]. 1991, 54(5): 1337-1344.
- [7] Gui R W, Yong L L, Wei D Z, *et al.* Cytotoxic terpenes from *Abies sibirica* [J]. *Chin Chem Lett*, 2012, 23(11): 1251-1253.
- [8] Lavoie S, Gauthier C, Legault J, *et al.* Lanostane-and cycloartane-type triterpenoids from *Abies balsamea* oleoresin. [J]. *Beilstein J Org Chem*, 2013, 9(13): 1333-1339.
- [9] Abdelmonem A R, Abdelsattar E, Harraz F M, *et al.* Chemical investigation of *Euphorbia schimperii* C. Presl [J]. *Rec Nat Prod*, 2008, 2(2): 39-45.
- [10] Entwistle N, Pratt A D. Artifacts of the acid treatment of (23S)-lanosta-8,24-diene-3 $\beta$ ,23-diol [J]. *Org Bio-Org Chem*, 1973, . doi: 10.1039/P19730001235
- [11] Yang X W, Feng L, Li S M, *et al.* Isolation, structure, and bioactivities of abiesadines A-Y, 25 new diterpenes from *Abies georgei* Orr [J]. *Bioorg Med Chem*, 2010, 18(2): 744-754.
- [12] Barrero A F, Sanchez J F, Alvarez E J. Endoperoxide diterpenoids and other constituents from *Abies marocana* [J]. *Phytochemistry*, 1991, 30(30): 593-597.
- [13] 芦毅, 华燕. 紫珠的松香烷型二萜成分研究 [J]. *天然产物研究与开发*, 2011, 23(1): 66-68.
- [14] Sircar J C, Fisher G S. Free-radical bromination of methyl abietate by *N*-bromosuccinimide and solvolysis of the products [J]. *J Org Chem*, 1970, 35(9): 3090-3093.
- [15] Cheung H T A, Miyase T, Lenguyen M P, *et al.* Further acidic constituents and neutral components of *Pinus massoniana* Resin [J]. *Tetrahedron*, 1993, 49(36): 7903-7915.
- [16] Fraga B, Mestres T, Diaz C E, *et al.* Dehydroabietane diterpenes from *Nepeta teydea* [J]. *Phytochemistry*, 1994, 35(6): 1509-1512.
- [17] Srivastava S, Kulshreshtha D K. Centdaroic acid, a new diterpene acid from *Cedrus deodara* [J]. *Indian J Chem Section B*, 2001, 40(4):348-349.
- [18] Bleif S, Hannemann F, Lisurek M, *et al.* Identification of CYP106A2 as a regioselective allylic bacterial diterpene hydroxylase [J]. *Chem Biol Chem*, 2011, 12(4): 576-582.
- [19] Zaidi S F H, Awale S, Kalauni S K, *et al.* Diterpenes from 'Pini resina' and their preferential cytotoxic activity under nutrient-deprived condition [J]. *Planta Med*, 2006, 72(13): 1231-1234.
- [20] Wu L, Li Y L, Li S M, *et al.* Systematic phytochemical investigation of *Abies spectabilis* [J]. *Chem Pharm Bull*, 2010, 58(12): 1646-1649.