

文章编号:1001-6880(2016)12-1870-06

海南红树植物角果木的二萜类化学成分研究

彭 媛,李敏一*

暨南大学药学院海洋药物研究中心,广州 510632

摘要:研究海南红树植物角果木的二萜类化学成分。通过硅胶、Sephadex LH-20 柱色谱以及高效液相色谱等分离纯化手段,从角果木醇提物中共分离得到 10 个二萜类化合物,运用现代波谱技术鉴定了它们的结构,分别为:($5S^*, 8S^*, 9S^*, 10R^*, 13S^*$)-2,16-dihydroxydolab-4R*,18-epoxy-3,15-dione (**1**)、tagalsin B (**2**)、*ent*-5 α ,2-oxodolab-3-ene-3,15,16-triol (**3**)、($5S^*, 8S^*, 9S^*, 10R^*$)-3,13S*-dihydroxy-15,16-dinorlab-3-en-2-one (**4**)、($5S^*, 8S^*, 9S^*, 10R^*, 13S^*$)-3-hydroxy-16-nor-2-oxodolab-3-ene-15-oic acid (**5**)、($5S^*, 8S^*, 9S^*, 10R^*$)-13S*,18-dihydroxy-15,16-dinordolab-4 (**18**)-ene-3-one (**6**)、($5S^*, 8S^*, 9S^*, 10R^*, 13S^*$)-18-hydroxy-16-nor-3-oxodolab-4 (**18**)-en-15-oic acid (**7**)、($5S^*, 8S^*, 9S^*, 10R^*$)-13S*-hydroxy-4S*,18-epoxy-15,16-dinordolab-1-en-3-one (**8**)、*ent*-8(**14**)-pimarane-16,18-dihydroxy-15-one (**9**)、*ent*-8(**14**)-pimarane-15,18-diol (**10**)。其中化合物 **1** 为新化合物,化合物 **3** 和 **5** 为首次从角果木中分离得到。

关键词:红树植物; 角果木; dolabrate 型二萜; 海松烷型二萜

中图分类号:R93

文献标识码:A

DOI:10.16333/j.1001-6880.2016.12.003

Diterpenoids from Hainan mangrove, *Ceriops tagal*

PENG Yuan, LI Min-yi*

Marine Drugs Research Center, College of Pharmacy, Jinan University, Guangzhou 510632, China

Abstract: The chemical constituents from the ethanol extract of *Ceriops tagal* were isolated and purified by column chromatography on silica gel, Sephadex LH-20 and HPLC. Their structures were identified by physical and spectral data. Ten diterpenoids were isolated and elucidated as ($5S^*, 8S^*, 9S^*, 10R^*, 13S^*$)-2,16-dihydroxydolab-4R*,18-epoxy-3,15-dione (**1**), tagalsin B (**2**), *ent*-5 α ,2-oxodolab-3-ene-3,15,16-triol (**3**), ($5S^*, 8S^*, 9S^*, 10R^*$)-3,13S*-dihydroxy-15,16-dinorlab-3-en-2-one (**4**), ($5S^*, 8S^*, 9S^*, 10R^*, 13S^*$)-3-hydroxy-16-nor-2-oxodolab-3-ene-15-oic acid (**5**), ($5S^*, 8S^*, 9S^*, 10R^*$)-13S*,18-dihydroxy-15,16-dinordolab-4 (**18**)-ene-3-one (**6**), ($5S^*, 8S^*, 9S^*, 10R^*, 13S^*$)-18-hydroxy-16-nor-3-oxodolab-4 (**18**)-en-15-oic acid (**7**), ($5S^*, 8S^*, 9S^*, 10R^*$)-13S*-hydroxy-4S*,18-epoxy-15,16-dinordolab-1-en-3-one (**8**), *ent*-8(**14**)-pimarane-16,18-dihydroxy-15-one (**9**), *ent*-8(**14**)-pimarane-15,18-diol (**10**)。Additionally, compound **1** was a new compound, and compounds **3** and **5** were obtained from *C. tagal* for the first time.

Key words: mangrove; *Ceriops tagal* (Perr.) C. B. Robinson; dolabrate-type diterpenoids; pimarane-type diterpenoids

角果木属 (*Ceriops*) 植物是生长在热带、亚热带海岸潮间带的红树科 (Rhizophoraceae) 真红树植物^[1]。该属植物全球有 5 个种,具体可分为 *C. tagal* complex(包括 *C. tagal* 和 *C. australis*) 和 *C. decandra* complex(包括 *C. decandra*、*C. pseudodecandra* 和 *C. zippeliana*)^[2]。角果木属植物在中国仅有一种,即角果木 (*C. tagal*),主要分布于海南岛^[3]。作

为一种药用植物,在我国民间,角果木的叶煎汁曾作为奎宁替代品治疗疟疾;在菲律宾,角果木树皮可以治疗产妇出血^[4-6]。

角果木的主要次生代谢产物是二萜和五环三萜^[7]。药理研究显示,从角果木中分离鉴定的二萜多数具有生物活性^[8]。其中,dolabrate 型二萜具有显著的抗肿瘤活性和良好的拒食活性,海松烷型二萜则具有较好的防污活性^[9-11]。为进一步寻找具有良好生物活性的药用先导化合物,本实验对产自中国海南的红树植物角果木的化学成分进行了较为系统地研究,从其醇提物中分离鉴定了 10 个二萜类化

收稿日期:2016-09-09 接受日期:2016-11-01

基金项目:国家自然科学基金面上项目(81473133);广州市珠江科技新星专项(2014J2200012)

* 通讯作者 Tel:86-20-85222050; E-mail:liminyi_jnu@163.com

合物(结构见图 1)。其中,化合物 1 为新 dolabrance 型二萜,化合物 3 和 5 为首次从角果木中分离得到。

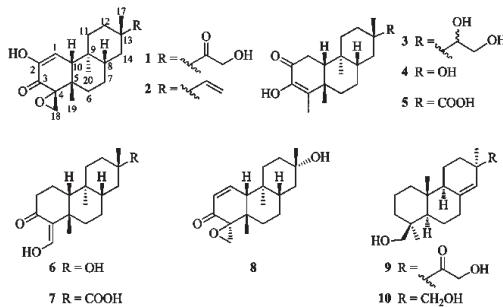


图 1 化合物 1~10 的结构

Fig. 1 Structures of compound 1-10

1 仪器与材料

正相硅胶(青岛海洋化工厂), Sephadex LH-20(瑞典 Pharmacia Biotech AB 公司), C₁₈ 反相硅胶(日本 YMC 公司), YMC C₁₈ 色谱柱(250 mm × 10 mm i.d., 5 μm, 半制备型; 250 mm × 4.5 mm i.d., 5 μm, 分析型), 高效液相色谱仪(美国 Waters 公司), AVANCE III 400 型核磁共振波谱仪(瑞士 Bruker 公司), AmaZon SL 离子阱电喷雾质谱仪(德国 Bruker Daltonics 公司)。色谱纯乙腈、甲醇(德国 Merck 公司), 分析纯丙酮、氯仿、甲醇、醋酸乙酯均重蒸。

海南红树角果木枝条于 2015 年 5 月采集于中国海南红树林湿地。由暨南大学海洋药物研究中心李敏一副教授鉴定为角果木 *Ceriops tagal* (Perr.) C. B. Robinson。样品标本保存于暨南大学药学院海洋药物研究中心。

2 提取与分离

将角果木枝条晾干、粉碎, 称重得 28.0 kg, 用 95% 的工业乙醇渗漉提取 3 次, 合并提取液, 减压浓缩得总浸膏 2305.9 g。将总浸膏用水混悬, 乙酸乙酯萃取 6 次, 回收溶剂得到乙酸乙酯萃取物 419.4 g。取 200.0 g 经正相硅胶柱层析分离, 氯仿-甲醇(100:1→5:1)梯度洗脱, TLC 分析后合并相同组分, 得到 9 个流分。

经 TLC 显色和高效液相色谱分析后, 对流分 2、5、8 进行进一步分离纯化。其中流分 2 经 Sephadex LH-20 凝胶柱层析, 氯仿-甲醇(1:1)洗脱除去色素, 再通过反相硅胶柱色谱分离, 丙酮-水(30:70→100:0)梯度洗脱, 得到 82 个流分(Fr. A. 1-Fr. A. 82)。

其中 Fr. A. 32 经高效液相色谱制备, 得到化合物 2(38.9 mg); 流分 5 先经 Sephadex LH-20 凝胶柱层析, 氯仿-甲醇(1:1)洗脱除去色素, 再通过反相硅胶柱色谱分离, 丙酮-水(30:70→100:0)梯度洗脱, 得到 90 个流分(Fr. B. 1-Fr. B. 90)。其中 Fr. B. 14-15 合并后经高效液相色谱制备得到化合物 8(6.2 mg)、Fr. B. 16 通过高效液相色谱二次制备得到化合物 1(3.6 mg)、Fr. B. 36 通过高效液相色谱二次制备得到化合物 5(6.0 mg) 和 6(4.1 mg)、Fr. B. 40 通过高效液相色谱制备得到化合物 9(8.0 mg)、Fr. B. 44~45 合并后经高效液相色谱制备并多次重结晶得到化合物 10(3.0 mg)、Fr. B. 24 和 Fr. B. 46 通过反复重结晶分别得到化合物 4(10.0 mg) 和 7(10.0 mg); 流分 8 经 Sephadex LH-20 凝胶柱层析, 氯仿-甲醇(1:1)洗脱, 通过 TLC 显色分析后, 得到脱去色素的 31 个流分(Fr. C. 1-Fr. C. 31), 其中 Fr. C. 12 经反复重结晶, 得到单体化合物 3(6.5 mg)。

3 结构鉴定

化合物 1 淡黄色油状物; $[\alpha]_D^{25}$ -155.6 (*c* 0.8, CH₃OH); UV(MeOH): λ_{max} = 204, 284 nm; IR(KBr) ν_{max} 3528, 3449, 2928, 1690, 1460, 1412, 1008 cm⁻¹。由 HR-ESI-MS 的准分子离子峰 *m/z* 349.1997 ([M + H]⁺, C₂₀H₂₉O₅, Δ*m* = 3.5 ppm), 确定该化合物分子式为 C₂₀H₂₈O₅, 不饱和度为 7。核磁数据(表 1)显示其中 3 个不饱和度分别来源于两个羰基(δ_c 215.1 qC; δ_c 192.1 qC)和一个双键(δ_c 147.8 qC; δ_c 118.4 CH), 因此该化合物存在 4 个环系。

根据 DEPT135 谱判断该化合物有 3 个甲基、7 个亚甲基、3 个次甲基和 7 个季碳。结合植物化学分类学知识和上述光谱信息可初步推测该化合物是一个 dolabrance 型二萜。一对独立的环氧质子信号(δ_H 3.12, d, *J* = 6.2 Hz; δ_H 3.10, d, *J* = 6.2 Hz)和 HMBC 相关信号(H₂-18/C-3, H₂-18/C-4, H₂-18/C-5; H₃-19/C-4, H-10/C-4)(图 2), 表明化合物 1 存在 4(18)位环氧结构, 其核磁数据与 tagalsin B(2)相似。两者的区别在于 C-13 位的取代基。Tagalsin B 的 C-13 位(δ_c 36.1)是双键取代, 化合物 1 缺少这对双键信号, 多出一个羟乙酰基信号(δ_H 4.39, s, 2H; δ_c 215.1, qC; δ_c 64.0, CH₂)。根据 H₃-17 与 C-13、C-15、C-12、C-14 之间的 HMBC 相关以及 H₂-16 与 C-15、C-13 之间的 HMBC 相关(图 2), 证实化合物 1 的 C-13(δ_c 45.6)上连接的是一个羟乙酰基。

该化合物的相对构型通过 NOE 谱(图 3)来确定,如 H-10/H₃-19、H-10/H-8、H-10/H-11 β 、H-11 β /17-CH₃之间的 NOE 相关表明 17-CH₃、H-8、19-CH₃、H-10 为 β 构型; H-6 α /20-CH₃ 相关表明 20-CH₃ 为 α 构型; H₃-19/H₂-18 相关表明 C-4 为 R 构型。综合以上分析,化合物 1 被鉴定为 (5S*, 8S*, 9S*, 10R*, 13S*)-2,16-dihydroxydolabrin-4R*, 18-epoxy-3,15-dione, 经各数据库检索确定其为新化合物。命名为角果木二萜 C。

表 1 化合物 1 的¹³C、¹H NMR 数据(CDCl₃, δ ppm, J in Hz)

Table 1 ¹³C NMR and ¹H NMR data of compound 1 in CDCl₃, δ in ppm, J in Hz

No.	δ_{C}	δ_{H}
1	118.4 d	6.27 (1H,d,6.7)
2	147.8 s	
3	192.1 s	
4	61.3 s	
5	37.3 s	
6	32.2 t	1.64 (1H,m); 1.19 (1H,m)
7	27.2 t	1.24 (2H,m)
8	39.7 d	1.50 (1H,m)
9	39.3 s	
10	54.8 d	2.22 (1H,d,6.7)
11	34.1 t	1.67 (1H,m); 1.43 (1H,m)
12	28.1 t	1.78 (1H,td,13.7,4.2); 1.47(1H,m)
13	45.6 s	
14	35.5 t	1.61 (1H,m); 1.31 (1H,dt,13.3,1.3)
15	215.1 s	
16	64.0 t	4.39 (2H,s)
17	20.4 q	1.27 (3H,s)
18	55.9 t	3.12 (1H,d,6.2); 3.10 (1H,d,6.2)
19	29.5 q	1.21 (3H,s)
20	13.2 q	0.76 (3H,s)
2-OH		5.98 br s

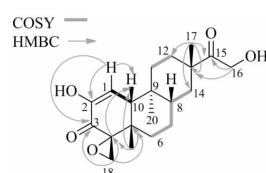


图 2 化合物 1 的主要 HMBC 和 COSY 相关

Fig. 2 Selected HMBC and COSY correlations for compound 1

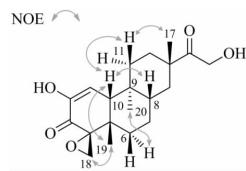


图 3 化合物 1 的主要 NOE 相关

Fig. 3 Diagnostic NOE interactions for compound 1

化合物 2 淡黄色晶体。¹H NMR (CDCl₃, 400 MHz) δ : 6.28 (1H, d, J = 6.7 Hz, H-1), 6.02 (1H, s, 3-OH), 5.76 (1H, dd, J = 17.5, 10.8 Hz, H-15), 4.89 (1H, dd, J = 17.5, 0.9 Hz, H-16 α), 2.83 (1H, dd, J = 10.8, 0.9 Hz, H-16 β), 3.10 (1H, d, J = 6.2 Hz, H-18a), 3.06 (1H, d, J = 6.2 Hz, H-18b), 2.19 (1H, d, J = 6.7 Hz, H-10), 1.56 (1H, m, H-6 α), 1.51 (1H, m, H-11 α), 1.46 (1H, m, H-12 α), 1.43 (1H, m, H-8), 1.39 (1H, m, H-11 β), 1.32 (1H, d, J = 13.2 Hz, H-14 α), 1.26 (1H, m, H-12 β), 1.21 (1H, m, H-7 α), 1.18 (3H, s, H-19), 1.03 (3H, s, H-17), 0.70 (3H, s, H-20), 1.17 (1H, m, H-7 β), 1.15 (1H, m, H-6 β), 1.07 (1H, dt, J = 13.6, 2.8 Hz, H-14 β); ¹³C NMR (CDCl₃, 100 MHz) δ : 119.0 (C-1), 147.2 (C-2), 191.9 (C-3), 61.1 (C-4), 36.9 (C-5), 32.0 (C-6), 27.1 (C-7), 40.0 (C-8), 39.1 (C-9), 54.7 (C-10), 34.6 (C-11), 31.5 (C-12), 36.1 (C-13), 39.2 (C-14), 150.4 (C-15), 108.9 (C-16), 22.6 (C-17), 55.5 (C-18), 29.2 (C-19), 12.9 (C-20)。以上数据与文献^[12]报道一致,故鉴定化合物 2 为 tagalsin B。

化合物 3 白色粉末。¹H NMR (CDCl₃, 400 MHz) δ : 6.11 (1H, s, 3 or 15 or 16-OH), 3.73 (1H, d, J = 10.3 Hz, H-16a), 3.51 (1H, t, J = 9.3 Hz, H-16b), 3.32 (1H, d, J = 8.1 Hz, H-15), 2.83 (1H, dd, J = 18.7, 6.4 Hz, H-1 β), 2.72 (1H, d, J = 18.5 Hz, H-1 α), 2.15 (1H, dt, J = 14.0, 2.7 Hz, H-6 α), 1.87 (3H, s, H-18), 1.23 (3H, s, H-19), 0.92 (3H, s, H-17), 0.60 (3H, s, H-20), 1.67 (1H, t, J = 3.5 Hz, H-11 α), 1.63 (1H, d, J = 5.3 Hz, H-10 β), 1.49 (1H, dd, J = 13.8, 4.1 Hz, H-12 α), 1.37 (1H, m, H-8 β), 1.34 (1H, m, H-14 α), 1.32 (1H, m, H-12 β), 1.28 (1H, m, H-6 β), 1.14 (1H, m, H-7 α), 1.10 (1H, m, H-7 β), 1.04 (1H, td, J = 13.0, 3.7 Hz, H-11 β), 0.87 (1H, d, J = 9.3 Hz, H-14 β); ¹³C NMR

(CDCl₃, 100 MHz) δ: 37.7 (C-1), 193.0 (C-2), 144.4 (C-3), 135.4 (C-4), 38.8 (C-5), 36.2 (C-6), 26.7 (C-7), 41.0 (C-8), 37.9 (C-9), 54.2 (C-10), 33.6 (C-11), 28.3 (C-12), 36.3 (C-13), 33.1 (C-14), 80.9 (C-15), 62.4 (C-16), 18.9 (C-17), 13.5 (C-18), 31.5 (C-19), 11.5 (C-20)。以上数据与文献^[13]报道一致,故鉴定化合物3为*ent*-5α,2-oxodolab-3-ene-3,15,16-triol。

化合物4 无色针晶。¹H NMR (CDCl₃, 400 MHz) δ: 6.12 (1H, s, 3-OH), 2.85 (1H, dd, *J* = 18.8, 6.5 Hz, H-1β), 2.70 (1H, d, *J* = 18.7 Hz, H-1α), 2.16 (1H, d, *J* = 13.6 Hz, H-6α), 1.86 (3H, s, H-18), 1.25 (3H, s, H-17), 1.22 (3H, s, H-19), 0.67 (3H, s, H-20), 1.76 (1H, d, *J* = 13.3 Hz, H-11α), 1.64 (1H, dd, *J* = 14.9, 5.5 Hz, H-12α), 1.60 (1H, s, H-10), 1.52 (1H, d, *J* = 4.8 Hz, H-12β), 1.48 (1H, m, H-14α), 1.32 (1H, d, *J* = 12.8 Hz, H-14β), 1.19 (1H, m, H-8), 1.19 (1H, m, H-7α), 0.95 (1H, td, *J* = 13.6, 4.0 Hz, H-11β); ¹³C NMR (CDCl₃, 100 MHz) δ: 33.7 (C-1), 193.2 (C-2), 144.8 (C-3), 135.7 (C-4), 39.2 (C-5), 38.2 (C-6), 26.9 (C-7), 44.6 (C-8), 38.2 (C-9), 54.7 (C-10), 36.6 (C-11), 35.8 (C-12), 71.4 (C-13), 42.8 (C-14), 27.2 (C-17), 11.9 (C-18), 31.9 (C-19), 14.2 (C-20)。以上数据与文献^[11]报道一致,故确定化合物4为(5S*, 8S*, 9S*, 10R*)-3, 13S*-dihydroxy-15, 16-dinorlabr-3-en-2-one, 俗名为tagalsin P。

化合物5 无色固体。¹H NMR (CDCl₃, 400 MHz) δ: 2.84 (1H, dd, *J* = 18.7, 6.4 Hz, H-1β), 2.71 (1H, d, *J* = 18.6 Hz, H-1α), 2.17 (1H, m, H-6α), 1.92 (1H, dd, *J* = 14.1, 4.2 Hz, H-12α), 1.87 (3H, s, H-18), 1.26 (3H, s, H-19), 1.23 (3H, s, H-17), 0.63 (3H, s, H-20), 1.73 (1H, d, *J* = 13.1 Hz, H-14α), 1.67 (1H, m, H-11α), 1.64 (1H, d, *J* = 5.8 Hz, H-10), 1.47 (1H, d, *J* = 14.5 Hz, H-12β), 1.36 (1H, m, H-8β), 1.30 (1H, m, H-14β), 1.17 (1H, d, *J* = 2.8 Hz, H-6β), 1.13 (1H, dd, *J* = 13.6, 3.1 Hz, H-7α), 1.06 (1H, td, *J* = 13.7, 4.1 Hz, H-11β); ¹³C NMR (100 MHz, CDCl₃) δ: 37.9 (C-1), 193.1 (C-2), 144.7 (C-3), 135.8 (C-4), 39.1 (C-5), 35.8 (C-6), 26.6 (C-7), 41.7 (C-8), 38.0 (C-9), 54.4 (C-10), 33.7 (C-11), 28.6 (C-12), 41.2 (C-13), 33.3 (C-14), 184.8 (C-15),

21.3 (C-17), 13.7 (C-18), 31.8 (C-19), 11.8 (C-20)。以上数据^[13]与文献报道一致,故鉴定化合物5为(5S*, 8S*, 9S*, 10R*, 13S*)-3-hydroxy-16-nor-2-oxodolab-3-ene-15-oic acid。

化合物6 透明油状物。¹H NMR (CDCl₃, 400 MHz) δ: 15.43 (1H, d, *J* = 7.7 Hz, 18-OH), 7.93 (1H, d, *J* = 7.7 Hz, H-18), 2.49 (2H, m, H-2), 2.15 (1H, m, H-6α), 2.11 (1H, m, H-1β), 1.97 (1H, m, H-1α), 1.76 (1H, dt, *J* = 13.4, 4.0 Hz, H-11α), 1.67 (1H, dd, *J* = 13.6, 4.3 Hz, H-12α), 1.54 (1H, m, H-12β), 1.48 (1H, m, H-14α), 1.41 (1H, m, H-6β), 1.33 (1H, m, H-14β), 1.28 (1H, m, H-8), 1.27 (1H, m, H-7α), 1.25 (3H, s, H-17), 1.15 (3H, s, H-19), 0.76 (3H, s, H-20), 1.21 (1H, m, H-10), 1.17 (1H, m, H-7β), 0.98 (1H, td, *J* = 13.5, 4.2 Hz, H-11β); ¹³C NMR (100 MHz, CDCl₃) δ: 16.6 (C-1), 31.6 (C-2), 199.7 (C-3), 116.8 (C-4), 36.3 (C-5), 36.9 (C-6), 25.5 (C-7), 45.4 (C-8), 37.8 (C-9), 51.9 (C-10), 37.6 (C-11), 35.8 (C-12), 71.4 (C-13), 42.8 (C-14), 27.0 (C-17), 171.4 (C-18), 35.9 (C-19), 13.1 (C-20)。以上数据与文献^[14]报道一致,故鉴定化合物6为(5S*, 8S*, 9S*, 10R*)-13S*, 18-dihydroxy-15, 16-dinordolab-4(18)-ene-3-one。

化合物7 白色粉末。¹H NMR (CDCl₃, 400 MHz) δ: 15.42 (1H, d, *J* = 7.8 Hz, 18-OH), 7.93 (1H, d, *J* = 7.8 Hz, H-18), 2.48 (2H, m, H-2), 2.15 (1H, m, H-6α), 2.09 (1H, m, H-1β), 1.98 (1H, m, H-1α), 1.92 (1H, dd, *J* = 14.1, 4.3 Hz, H-12α), 1.72 (1H, m, H-11α), 1.69 (1H, m, H-14α), 1.48 (1H, m, H-12β), 1.43 (1H, m, H-6β), 1.38 (1H, m, H-8), 1.29 (1H, m, H-14β), 1.26 (3H, s, H-17), 1.15 (3H, s, H-19), 0.73 (3H, s, H-20), 1.24 (1H, m, H-7α), 1.22 (1H, m, H-10), 1.12 (1H, m, H-7β), 1.07 (1H, m, H-11β); ¹³C NMR (CDCl₃, 100 MHz) δ: 16.2 (C-1), 31.6 (C-2), 199.6 (C-3), 116.7 (C-4), 36.3 (C-5), 36.7 (C-6), 25.4 (C-7), 42.2 (C-8), 37.7 (C-9), 51.8 (C-10), 34.8 (C-11), 28.7 (C-12), 41.8 (C-13), 35.8 (C-14), 184.9 (C-15), 21.3 (C-17), 171.5 (C-18), 36.0 (C-19), 12.7 (C-20)。以上数据与文献^[11]报道一致,故鉴定化合物7为(5S*, 8S*, 9S*, 10R*, 13S*)-18-hydroxy-16-nor-3-oxodolab-4(18)-ene-15-

oic acid,俗名为 tagalsin R。

化合物 8 白色固体。¹H NMR (CDCl₃, 400 MHz) δ: 7.03 (1H, dd, *J* = 10.3, 6.0 Hz, H-1), 6.25 (1H, dd, *J* = 10.3, 1.0 Hz, H-2), 3.02 (1H, d, *J* = 6.3 Hz, H-18a), 2.99 (1H, d, *J* = 6.3 Hz, H-18b), 2.16 (1H, d, *J* = 6.0 Hz, H-10), 1.65 (1H, m, H-11α), 1.62 (1H, m, H-6α), 1.58 (1H, m, H-12α), 1.55 (1H, m, H-12β), 1.44 (1H, d, *J* = 12.6 Hz, H-14α), 1.26 (3H, s, H-17), 1.14 (3H, s, H-19), 0.77 (3H, s, H-20), 1.39 (1H, m, H-14β), 1.32 (1H, m, H-11β), 1.28 (1H, m, H-8), 1.22 (2H, m, H-7), 1.10 (1H, m, H-6β); ¹³C NMR (CDCl₃, 100 MHz) δ: 150.2 (C-1), 129.9 (C-2), 194.7 (C-3), 61.0 (C-4), 36.4 (C-5), 31.5 (C-6), 26.9 (C-7), 42.6 (C-8), 38.4 (C-9), 57.5 (C-10), 36.7 (C-11), 35.2 (C-12), 70.4 (C-13), 42.6 (C-14), 26.2 (C-17), 54.8 (C-18), 28.8 (C-19), 12.9 (C-20)。以上数据与文献^[15]报道一致,故鉴定化合物 8 为(5*S*^{*}, 8*S*^{*}, 9*S*^{*}, 10*R*^{*})-13*S*^{*}-hydroxy-4*S*^{*}, 18-epoxy-15, 16-dinordolab-1-en-3-one,俗名为 tagalsin W。

化合物 9 淡黄色固体。¹H NMR (CDCl₃, 400 MHz) δ: 5.36 (1H, d, *J* = 1.6 Hz, H-14), 4.33 (2H, s, H-16), 3.77 (1H, d, *J* = 10.8 Hz, H-18a), 3.41 (1H, d, *J* = 10.7 Hz, H-18b), 2.34 (1H, m, H-7α), 2.29 (1H, m, H-12β), 2.04 (1H, dddd, *J* = 13.6, 5.9, 3.8, 1.6 Hz, H-7β), 1.83 (1H, m, H-3β), 1.76 (1H, m, H-9), 1.72 (1H, m, H-6β), 1.64 (1H, m, H-6α), 1.62 (1H, m, H-1β), 1.58 (1H, m, H-11β), 1.45 (1H, m, H-2α), 1.41 (1H, m, H-2β), 1.22 (1H, dd, *J* = 12.9, 2.2 Hz, H-5), 1.13 (1H, m, H-12α), 1.11 (3H, s, H-17), 0.98 (3H, s, H-19), 0.60 (3H, s, H-20), 1.08 (1H, m, H-11α), 1.03 (1H, m, H-1α), 0.94 (1H, m, H-3α); ¹³C NMR (100 MHz, CDCl₃) δ: 38.8 (C-1), 18.5 (C-2), 35.3 (C-3), 38.5 (C-4), 55.6 (C-5), 22.3 (C-6), 36.1 (C-7), 142.5 (C-8), 51.0 (C-9), 38.4 (C-10), 20.3 (C-11), 32.7 (C-12), 46.8 (C-13), 123.2 (C-14), 214.7 (C-15), 65.8 (C-16), 27.4 (C-17), 65.0 (C-18), 27.0 (C-19), 15.5 (C-20)。以上数据与文献^[16]报道一致,故鉴定化合物 9 为 *ent*-8(14)-pimaran-16, 18-dihydroxy-15-one。

化合物 10 白色固体。¹H NMR (CDCl₃, 400 MHz) δ: 5.11 (1H, s, H-14), 3.81 (1H, d, *J* = 10.8

Hz, H-18a), 3.42 (1H, d, *J* = 3.7 Hz, H-15b), 3.40 (1H, d, *J* = 4.1 Hz, H-15a), 3.30 (1H, d, *J* = 10.7 Hz, H-18b), 2.27 (1H, ddd, *J* = 14.3, 4.1, 1.9 Hz, H-7α), 2.02 (1H, m, H-7β), 1.84 (1H, m, H-3β), 1.74 (1H, m, H-9), 1.71 (1H, m, H-6β), 1.69 (1H, m, H-1β), 1.67 (1H, m, H-12β), 1.57 (1H, m, H-2α), 1.47 (2H, m, H-11), 1.41 (1H, m, H-2β), 1.28 (1H, m, H-6α), 1.21 (1H, m, H-5), 1.10 (1H, td, *J* = 13.0, 4.0 Hz, H-12α), 1.02 (1H, m, H-1α), 0.98 (3H, s, H-19), 0.93 (3H, s, H-17), 0.72 (3H, s, H-20), 0.95 (1H, m, H-3α); ¹³C NMR (100 MHz, CDCl₃) δ: 39.4 (C-1), 18.8 (C-2), 35.5 (C-3), 38.7 (C-4), 56.0 (C-5), 22.5 (C-6), 36.5 (C-7), 139.8 (C-8), 51.0 (C-9), 38.2 (C-10), 19.2 (C-11), 31.4 (C-12), 36.5 (C-13), 127.6 (C-14), 70.0 (C-15), 25.8 (C-17), 65.3 (C-18), 27.2 (C-19), 16.0 (C-20)。以上数据与文献^[16]报道一致,故鉴定化合物 10 为 *ent*-8(14)-pimaran-15, 18-diol。

参考文献

- Wu J, Xiao Q, Xu J, et al. Natural products from true mangrove flora: source, chemistry and bioactivities. *Nat Prod Rep*, 2008, 25: 955-981.
- Tsai CC, Li SJ, Su YY, et al. Molecular phylogeny and evidence for natural hybridization and historical introgression between *Ceriops* species (Rhizophoraceae). *Biochem Syst Ecol*, 2012, 43: 178-191.
- Liao BW(廖宝文), Zhang QM(张乔民). Area, distribution and species composition of mangroves in China. *Wetland Sci* (湿地科学), 2014, 12: 435-440.
- Wang H, Li MY, Wu J. Chemical constituents and some biological activities of plants from the genus *Ceriops*. *Chem Biodivers*, 2012, 9(1): 1-11.
- He L(何磊), Wang YS(王友绍), Wang QJ(王清吉), et al. Study on chemical constituents of *Ceriopstagal*. *Chin Pharm J*(中国药学杂志), 2006, 41: 341-343.
- Bamroongrugsa N. Bioactive substances from the mangrove resource. *Songklanakarin J Sci Technol*, 1999, 21: 377-386.
- Chen JD(陈俊德). The chemical constituents and antifouling activities of the mangrove plant *Ceriopstagal*. Xiamen: Xiamen University(厦门大学), PhD. 2012.
- Eric WCC, Joseph T, Mio K, et al. Botany, uses, chemistry and bioactivities of mangrove plants II: *Ceriopstagal*. *IsmeGloris Elect J*, 2015, 13(6): 39-43.

(下转第 1970 页)