云南红豆杉种子的化学成分研究

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摘　要：目的　研究云南红豆杉 *Taxus yunnanensis* 种子的化学成分。**方法**　通过色谱技术进行分离纯化，利用核磁共振技术鉴定化合物的结构。**结果**　从云南红豆杉种子中分离得到 12 个紫杉烷类化合物，分别鉴定为 7-表-10-去乙酰基紫杉醇（**1**）、9α, 10β-二乙酰基-2α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮（**2**）、2α, 7α, 10β-三乙酰基-9α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮（**3**）、2α-乙酰基-9α, 10β-二羟基-5α-桂皮酰基紫杉烷-4(20), 11-二烯-13-酮（**4**）、2α, 7β, 9α, 10β-四乙酰基-5α-桂皮酰基-11, 12-环氧紫杉烷-4(20)-烯-13-酮（**5**）、7β, 9α, 10β-三乙酰基-5α-桂皮酰基紫杉烷-4(20), 11-烯-13α-醇（**6**）、9-去乙酰基紫杉宁 A（**7**）、5α-去桂皮酰基紫杉欧吉酚（**8**）、2α, 5α, 10β, 13α-四乙酰基-1β, 7β, 9α-三羟基-4, 20-环氧紫杉烷-11-烯（**9**）、7β, 9α, 10β-三乙酰基-2α, 5α, 13α-三羟基紫杉烷-4(20), 11-二烯（**10**）、7, 9, 10, 13-tetra-*O*-deacetylabeobaccatin VI（**11**）、taxacustin（**12**）。**结论**　化合物 **2**、**3**、**7**～**12** 为首次从该植物中分离得到。

关键词：云南红豆杉；紫杉烷；9α, 10β-二乙酰基-2α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮；9-去乙酰基紫杉宁 A；5α-去桂皮酰基紫杉欧吉酚

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Chemical constituents from seeds of *Taxus yunnanensis*

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Abstract: Objective　To study the chemical constituents from the seeds of *Taxus yunnanensis*. **Methods**　The chemical constituents in the seeds of *T. yunnanensis* were isolated by chromatography and identified by a comprehensive analysis on the spectral data. **Results**　Twelve taxanes were isolated from the seeds of *T. yunnanensis* and identified as 7-*epi*-10-deacetyltaxol (**1**), 2-deacetoxytaxuspine C (**2**), 9α-hydroxy-2α, 7α, 10β-triacetoxy-5α-cinnamoyloxy-3, 11-cyclotaxa-4(20)-en-13-one (**3**), 2α-acetoxy-5α-cinnamoyloxy-9α, 10β-dihydroxy-taxa-4 (20), 11-diene-13-one (**4**), dantaxusin C (**5**), taxezopidine H (**6**), 9-deacetyltaxinine A (**7**), 5α-decinnamoyltaxagifine (**8**), taxumairol B (**9**), 2α, 5α, 13α-trihydroxy-7β, 9α, 10β-triacetoxy-taxa-4(20), 11-diene (**10**), 7, 9, 10, 13-tetra-*O*-deacetylabeobaccatin VI (**11**), and taxacustin (**12**). **Conclusion**　Compounds **2**, **3**, and **7**—**12** are isolated from *T. yunnanensis* for the first time.

Key words: *Taxus yunnanensis* W. C. Cheng & L. K. Fu; taxanes; 2-deacetoxytaxuspine C; 9-deacetyltaxinine A; 5α-decinnamoyltaxagifine

紫杉醇以其独特的抗肿瘤作用机制和对卵巢癌、乳腺癌、Kaposi's 综合征的神奇疗效，一直是全世界药物工作者的研究热点。由于紫杉醇在树皮中的量极低，药源供应紧缺，研究者们对红豆杉属的其他种植物进行了大量的研究，希望从中发现新的紫杉醇类似物，或找到紫杉醇的生物合成前体，从而扩大紫杉醇的药源或寻找开发出新的紫杉烷类抗癌活性成分。尽管文献报道紫杉烷类化合物

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已达到 560 多个[1]，但是新的紫杉烷类化合物仍然不断地被发现[2-3]。云南红豆杉 *Taxus yunnanensis* W. C. Cheng & L. K. Fu 主要分布在云南省保山市、腾冲县，滇西北的大理、中甸、丽江、维西一带，是我国生产紫杉醇的主要树种。目前对其化学成分研究主要涉及到树皮、心材、枝和叶，对种子化学成分的研究还未见报道。本课题组长期进行紫杉烷类化学成分研究，从云南红豆杉种子中分离得到 12 个紫杉烷类化合物，分别鉴定为 7-表-10-去乙酰基紫杉醇（7-*epi*-10-deacetyltaxol，**1**）、9α, 10β-二乙酰基-2α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮（2-deacetoxytaxuspine C，**2**）、2α, 7α, 10β-三乙酰基-9α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮 [9α-hydroxy-2α, 7α, 10β-triacetoxy-5α-cinnamoyloxy-3, 11-cyclotaxa-4(20)-en-13-one，**3**]、2α-乙酰基-9α, 10β-二羟基-5α-桂皮酰基紫杉烷-4(20), 11-二烯-13-酮 [2α-acetoxy-5α-cinnamoyloxy-9α, 10β-dihydroxy-taxa-4(20), 11-diene-13-one，**4**]、2α, 7β, 9α, 10β-四乙酰基-5α-桂皮酰基-11, 12-环氧紫杉烷-4(20)-烯-13-酮（dantaxusin C，**5**）、7β, 9α, 10β-三乙酰基-5α-桂皮酰基紫杉烷-4(20), 11-烯-13α-醇（taxezopidine H，**6**）、9-去乙酰基紫杉宁 A（9-deacetyltaxinine A，**7**）、5α-去桂皮酰基紫杉欧吉酚（5α-decinnamoyltaxagifine，**8**）、2α, 5α, 10β, 13α-四乙酰基-1β, 7β, 9α-三羟基-4, 20-环氧紫杉烷-11-烯（taxumairol B，**9**）、7β, 9α, 10β-三乙酰基-2α, 5α, 13α-三羟基紫杉烷-4(20), 11-二烯 [2α, 5α, 13α-trihydroxy-7β, 9α, 10β-triacetoxy-taxa-4(20), 11-diene，**10**]、7, 9, 10, 13-tetra-*O*-deacetylabeobaccatin VI（**11**）、taxacustin（**12**）。其中化合物 **2**、**3**、**7**～**12** 为首次从该植物中分离得到。

1 仪器与材料

Bruker Advance—500 核磁共振仪测定（瑞士布鲁克公司）；薄层色谱和柱色谱用硅胶均为青岛海洋化工厂生产。薄层显色剂为 10% H_2SO_4 乙醇溶液，喷雾后加热显色。

药材于 2009 年采自云南保山，经河北医科大学王建华教授鉴定为云南红豆杉 *Taxus yunnanensis* W. C. Cheng & L. K. Fu 的种子。样品（2009-10）现保存于河北医科大学药学院生药标本室。

2 提取与分离

取粉碎后种子约 2.2 kg，用 95%乙醇冷浸提取，每次浸泡时间为 7 d，共提取 3 次。合并提取液浓缩得浸膏约 120 g。将浸膏分散于蒸馏水中并加入适量的 NaCl 使达饱和，石油醚脱脂后，醋酸乙酯萃取 3 次，所得醋酸乙酯萃取液分别用 5% HCl 水溶液和 5% Na_2CO_3 水溶液萃取处理后，得到云南红豆杉种子的碱性部位约 2.2 g、酚性部位约 2.4 g 及中性部位约 52 g。碱性部位采用硅胶柱色谱法进行分离，二氯甲烷-甲醇（9∶1）洗脱，收集流出液，薄层检识合并后，得到 15 个流分 Fr. 1～15。Fr. 11 中析出白色粉末状固体，为化合物 **1**（10 mg）。中性部位采用硅胶柱色谱法进行分离，石油醚-醋酸乙酯（9∶1、8∶2、7∶3、6∶4、1∶1、2∶3）梯度洗脱，收集各流出液，薄层检识合并后，得到 15 个流分 Fr. 1～15。其中 Fr. 1 析出白色固体，经丙酮重结晶后得到化合物 **2**（12 mg）。中性部位 Fr. 2 浓缩过程中析出白色固体，经丙酮重结晶后得到化合物 **3**（8 mg）。浓缩后采用硅胶柱色谱进行分离，石油醚-醋酸乙酯（9∶1、8∶2、7∶3）梯度洗脱，得到化合物 **4**（12 mg）和 **5**（10 mg）；中性部位 Fr. 2 母液进行柱色谱分离得到 Fr. 2-2～2-5，再经制备高效液相色谱分离，流动相为乙腈-水（60∶40），得到化合物 **6**（7 mg）。中性部位 Fr. 4～6 合并后采用硅胶柱色谱进行分离，二氯甲烷-丙酮（8∶2、7∶3、6∶4）梯度洗脱，薄层检识合并，共得到 14 个流分，分别经 Sephadex LH-20 色谱，甲醇洗脱纯化后，得化合物 **7**（15 mg）、**8**（12 mg）和 **9**（10 mg）。中性部位 Fr. 10 硅胶柱色谱进行分离，二氯甲烷-丙酮（8∶2、7∶3、1∶1）梯度洗脱，共得到 10 个流分。分别经 Sephadex LH-20 色谱，甲醇洗脱纯化后，得化合物 **10**（15 mg）、**11**（12 mg）和 **12**（10 mg）。

3 结构鉴定

化合物 **1**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 5.73 (1H, d, J = 7.4 Hz, H-2), 3.91 (1H, d, J = 7.4 Hz, H-3), 4.90 (1H, dd, J = 9.0, 3.9 Hz, H-5), 2.32 (2H, m, H-6a, 6b), 3.66 (1H, brdd, J = 12.2, 4.8 Hz, H-7), 4.73 (1H, s, 7-OH), 5.42 (1H, s, H-10), 4.11 (1H, s, 10-OH), 6.23 (1H, m, H-13), 2.38 (1H, m, H-14a), 2.22 (1H, m, H-14b), 1.20 (3H, s, H-16), 1.08 (3H, s, H-17), 1.74 (3H, s, H-18), 1.72 (3H, s, H-19), 4.39 (2H, s, H-20), 8.16 (2H, d, J = 7.7 Hz, Bz-H-2′, 6′), 7.52 (2H, t, J = 7.9 Hz, Bz-H-3′, 5′), 7.61 (1H, t, J = 7.5 Hz, Bz-H-4′), 4.79 (1H, brs, H-2′), 3.44 (1H, brs, 2′-OH), 5.79 (1H, dd, J = 9.2, 2.7 Hz, H-3′), 7.37～7.72 (5H, m, Ar-H-1″~5″)；^{13}C-NMR

(125 MHz, $CDCl_3$) δ: 79.1 (C-1), 75.4 (C-2), 40.3 (C-3), 81.9 (C-4), 82.6 (C-5), 35.4 (C-6), 75.8 (C-7), 57.1 (C-8), 214.9 (C-9), 77.7 (C-10), 135.5 (C-11), 137.7 (C-12), 72.5 (C-13), 36.3 (C-14), 42.4 (C-15), 26.0 (C-16), 20.5 (C-17), 14.3 (C-18), 16.6 (C-19), 77.7 (C-20), 22.5, 172.3 ($OCOCH_3$), 166.9 (Ar-CO), 126.5～128.6 (Ar-C), 73.1 (C-2′), 54.9 (C-3′), 166.9 (5′-CO)。以上数据与文献报道一致[4]，故鉴定化合物 **1** 为 7-表-10-去乙酰基紫杉醇。

化合物 **2**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.01 (1H, m, H-1), 5.15 (1H, d, J = 4.9 Hz, H-2), 5.61 (1H, m, H-5), 2.19 (1H, m, H-6a), 1.77 (1H, m, H-6b), 1.78 (1H, m, H-7a), 1.28 (1H, m, H-7b), 5.69 (1H, d, J = 9.7 Hz, H-9), 5.62 (1H, d, J = 9.7 Hz, H-10), 3.50 (1H, q, J = 7.2 Hz, H-12), 2.79 (1H, d, J = 20.6 Hz, H-14a), 2.50 (1H, dd, J = 20.6, 7.7 Hz, H-14b), 1.20 (3H, s, 16-CH_3), 1.60 (3H, s, 17-CH_3), 1.27 (3H, s, 18-CH_3), 1.40 (3H, s, 19-CH_3), 5.89 (1H, s, H-20a), 5.68 (1H, s, H-20b), 2.05, 2.04 (各 3H, s, 2×$OCOCH_3$), 6.39 (1H, d, J = 16.1 Hz, H-2′), 7.67 (1H, d, J = 16.1 Hz, H-3′), 7.55 (2H, m, H-5′, 9′), 7.37 (3H, m, H-6′～8′)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 50.6 (C-1), 75.7 (C-2), 66.4 (C-3), 142.9 (C-4), 76.1 (C-5), 25.6 (C-6), 31.0 (C-7), 44.4 (C-8), 82.1 (C-9), 79.4 (C-10), 58.4 (C-11), 51.8 (C-12), 215.3 (C-13), 38.2 (C-14), 42.7 (C-15), 26.6 (C-16), 29.0 (C-17), 15.5 (C-18), 25.6 (C-19), 127.9 (C-20), 166.0 (C-1′), 117.7 (C-2′), 145.3 (C-3′), 134.5 (C-4′), 128.1 (C-5′, 9′), 128.7 (C-6′, 8′), 130.1 (C-7′), 21.0 (9, 10-$OCOCH_3$), 169.8, 171.0 (9, 10-$OCOCH_3$)。以上数据与文献报道一致[5]，故鉴定化合物 **2** 为 9α, 10β-二乙酰基-2α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮。

化合物 **3**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.15 (1H, m, H-1), 6.05 (1H, d, J = 5.5 Hz, H-2), 5.71 (1H, t, J = 9.8 Hz, H-5), 2.67 (1H, ddd, J = 15.2, 10.4, 4.6 Hz, H-6a), 2.01 (1H, ddd, J = 15.2, 8.8, 1.5 Hz, H-6b), 5.32 (1H, dd, J = 4.6, 1.5 Hz, H-7b), 4.52 (1H, dd, J = 9.4, 2.5 Hz, H-9), 3.29 (1H, d, J = 2.5 Hz, 9-OH), 5.34 (1H, d, J = 9.4 Hz, H-10), 3.62 (1H, q, J = 7.7 Hz, H-12), 2.62 (1H, d, J = 20.5 Hz, H-14a), 2.52 (1H, dd, J = 20.5, 6.8 Hz, H-14b), 1.24 (3H, s, 16-CH_3), 1.55 (3H, s, 17-CH_3), 1.33 (3H, s, 18-CH_3), 1.42 (3H, s, 19-CH_3), 5.84 (1H, s, H-20a), 5.70 (1H, s, H-20b), 2.16 (3H, s, -$OCOCH_3$), 2.08 (3H, s, -$OCOCH_3$), 1.95 (3H, s, -$OCOCH_3$), 6.34 (1H, d, J = 16.0 Hz, H-2′), 7.66 (1H, d, J = 16.0 Hz, H-3′), 7.54 (2H, m, H-5′, 9′), 7.38 (3H, m, H-6′～8′)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 48.2 (C-1), 75.9 (C-2), 65.7 (C-3), 141.6 (C-4), 74.0 (C-5), 30.8 (C-6), 73.5 (C-7), 48.7 (C-8), 83.6 (C-9), 84.8 (C-10), 58.1 (C-11), 52.5 (C-12), 214.2 (C-13), 38.8 (C-14), 42.9 (C-15), 27.0 (C-16), 28.9 (C-17), 15.9 (C-18), 24.8 (C-19), 128.4 (C-20), 165.3 (C-1′), 117.5 (C-2′), 145.2 (C-3′), 134.1 (C-4′), 128.2 (C-5′, 9′), 128.9 (C-6′, 8′), 130.3 (C-7′), 21.3, 21.3, 20.9 (2, 7, 10-$OCOCH_3$), 169.2, 169.7, 172.6 (2, 7, 10-$OCOCH_3$)。以上数据与文献报道一致[6]，故鉴定化合物 **3** 为 2α, 7α, 10β-三乙酰基-9α-羟基-5α-桂皮酰基-3, 11-环化紫杉烷-4(20)-烯-13-酮。

化合物 **4**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.14 (1H, m, H-1), 5.51 (1H, dd, J = 6.2, 1.8 Hz, H-2), 3.36 (1H, d, J = 6.2 Hz, H-3), 5.32 (1H, t, J = 2.7 Hz, H-5), 1.97 (1H, m, H-6a), 1.74 (1H, m, H-6b), 1.79 (1H, m, H-7a), 1.50 (1H, m, H-7b), 1.18 (1H, d, J = 9.1 Hz, H-9), 4.89 (1H, d, J = 9.1 Hz, H-10), 2.83 (1H, dd, J = 20.0, 7.0 Hz, H-14a), 2.42 (1H, d, J = 20.0 Hz, H-14b), 1.22 (3H, s, 16-CH_3), 1.70 (3H, s, 17-CH_3), 2.16 (3H, s, 18-CH_3), 1.10 (3H, s, 19-CH_3), 5.31 (1H, s, H-20a), 4.84 (1H, s, H-20b), 2.06 (3H, s, 2-$OCOCH_3$), 6.43 (1H, d, J = 16.0 Hz, H-2′), 7.64 (1H, d, J = 16.0 Hz, H-3′), 7.75 (2H, d, J = 7.5 Hz, H-5′, 9′), 7.44 (1H, t, J = 7.5 Hz, H-6′, 8′), 7.39 (1H, m, H-7′)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 48.8 (C-1), 69.6 (C-2), 43.0 (C-3), 142.8 (C-4), 78.5 (C-5), 28.3 (C-6), 26.2 (C-7), 44.7 (C-8), 77.6 (C-9), 73.2 (C-10), 155.5 (C-11), 136.2 (C-12), 200.0 (C-13), 36.1 (C-14), 38.7 (C-15), 37.4 (C-16), 25.1 (C-17), 13.9 (C-18), 17.6 (C-19), 116.4 (C-20), 166.6 (C-1′), 117.8 (C-2′), 145.4 (C-3′), 134.7 (C-4′), 128.2 (C-5′, 9′), 128.7 (C-6′, 8′), 130.3 (C-7′), 21.4, 170.0 ($OCOCH_3$)。以上数据与文献报道一致[7]，故鉴定化合物 **4** 为 2α-乙酰基-9α, 10β-二羟基-5α-桂皮酰基紫杉烷-4(20), 11-二烯-13-酮。

化合物 **5**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.98 (1H, dd, J =8.6, 1.8 Hz,

H-1), 5.77 (1H, dd, *J* =6.0, 1.8 Hz, H-2), 3.07 (1H, d, *J* = 6.0 Hz, H-3), 5.52 (1H, dd, *J* =2.0, 3.9 Hz, H-5), 2.14 (1H, m, H-6a), 1.84 (1H, m, H-6b), 5.64 (1H, dd, *J* = 11.5, 5.6 Hz, H-7), 6.02 (1H, d, *J* = 11.0 Hz, H-9), 5.46 (1H, d, *J* = 11.0 Hz, H-10), 2.68 (1H, dd, *J* = 20.2, 8.6 Hz, H-14a), 2.34 (1H, d, *J* = 20.2 Hz, H-14b), 0.82 (3H, s, 16-CH_3), 1.83 (3H, s, 17-CH_3), 2.10 (3H, s, 18-CH_3), 1.07 (3H, s, 19-CH_3), 5.57 (1H, s, H-20a), 5.10 (1H, s, H-20b), 2.06 (3H, s, 2-$OCOCH_3$), 2.04 (3H, s, 7-$OCOCH_3$), 2.13 (3H, s, 9-$OCOCH_3$), 2.03 (3H, s, 10-$OCOCH_3$), 6.23 (1H, d, *J* = 15.9 Hz, H-2′), 7.69 (1H, d, *J* = 15.9 Hz, H-3′), 7.64 (2H, m, H-5′, 9′), 7.44 (3H, m, H-6′～8′); ^{13}C-NMR (125 MHz, $CDCl_3$) *δ*: 51.3 (C-1), 68.2 (C-2), 41.8 (C-3), 138.6 (C-4), 76.2 (C-5), 34.6 (C-6), 68.8 (C-7), 46.8 (C-8), 75.3 (C-9), 71.2 (C-10), 64.3 (C-11), 59.2 (C-12), 208.2 (C-13), 38.1 (C-14), 38.3 (C-15), 28.9 (C-16), 25.4 (C-17), 15.3 (C-18), 13.5 (C-19), 120.6 (C-20), 165.7 (C-1′), 116.4 (C-2′), 147.0 (C-3′), 134.0 (C-4′), 128.5 (C-5′, 9′), 129.2 (C-6′, 8′), 130.6 (C-7′), 21.2～20.5 (4×$OCOCH_3$), 169.2～170.4 (4×$OCOCH_3$)。以上数据与文献报道一致[8]，故鉴定化合物**5**为2α, 7β, 9α, 10β-四乙酰基-5α-桂皮酰基-11, 12-环氧紫杉烷- 4(20)-烯-13-酮。

化合物 **6**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) *δ*: 1.78 (1H, m, H-1), 1.90 (1H, m, H-2a), 1.78 (1H, m, H-2b), 3.05 (1H, d, *J* = 5.6 Hz, H-3), 5.52 (1H, dd, *J* =2.3, 3.7 Hz, H-5), 2.05 (1H, m, H-6a), 1.78 (1H, m, H-6b), 5.63 (1H, dd, *J* = 11.7, 5.0 Hz, H-7), 5.86 (1H, d, *J* = 11.0 Hz, H-9), 6.26 (1H, d, *J* = 11.0 Hz, H-10), 4.53 (1H, brdd, *J* = 9.7, 5.2 Hz, H-13), 2.81 (1H, dd, *J* = 15.5, 5.2 Hz, H-14a), 1.10 (1H, dd, *J* = 15.5, 5.2 Hz, H-14b), 0.96 (3H, s, 16-CH_3), 1.56 (3H, s, 17-CH_3), 2.39 (3H, s, 18-CH_3), 0.85 (3H, s, 19-CH_3), 5.34 (1H, s, H-20a), 5.00 (1H, s, H-20b), 2.05 (3H, s, 7-OAc), 2.02 (3H, s, 9-OAc), 1.98 (3H, s, 10-OAc), 6.68 (1H, d, *J* = 15.9 Hz, H-2′), 7.70 (1H, d, *J* = 15.9 Hz, H-3′), 7.53 (2H, m, H-5′, 9′), 7.37 (3H, m, H-6′～8′); ^{13}C-NMR (125 MHz, $CDCl_3$) *δ*: 40.1 (C-1), 27.2 (C-2), 37.7 (C-3), 146.5 (C-4), 75.0 (C-5), 34.0 (C-6), 69.9 (C-7), 46.3 (C-8), 76.7 (C-9), 72.3 (C-10), 134.3 (C-11), 141.8 (C-12), 67.9 (C-13), 36.4 (C-14), 38.8 (C-15), 31.8 (C-16), 26.5 (C-17), 16.0 (C-18), 13.0 (C-19), 115.7 (C-20), 166.2 (C-1′), 117.6 (C-2′), 146.6 (C-3′), 134.3 (C-4′), 128.2 (C-5′, 9′), 129.0 (C-6′, 8′), 130.4 (C-7′), 21.2, 20.7, 20.9 (3×$OCOCH_3$), 169.2, 169.6, 170.1 (3×$OCOCH_3$)。以上数据与文献报道一致[9]，故鉴定化合物**6**为7β, 9α, 10β-三乙酰基-5α-桂皮酰基紫杉烷-4(20), 11-烯-13α-醇。

化合物 **7**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) *δ*: 2.09 (1H, dd, *J* = 7.1, 1.9 Hz, H-1), 5.47 (1H, dd, *J* = 5.9, 1.9 Hz, H-2), 3.56 (1H, d, *J* = 5.9 Hz, H-3), 4.17 (1H, t, *J* = 2.5 Hz, H-5), 1.76 (1H, m, H-6a), 1.62 (1H, m, H-6b), 1.70 (1H, m, H-7), 4.28 (1H, d, *J* = 9.6 Hz, H-9), 5.88 (1H, d, *J* = 9.6 Hz, H-10), 2.75 (1H, dd, *J* = 19.6, 7.1 Hz, H-14a), 2.34 (1H, d, *J* = 7.1 Hz, H-14b), 1.11 (3H, s, 16-CH_3), 1.63 (3H, s, 17-CH_3), 2.21 (3H, s, 18-CH_3), 1.06 (3H, s, 19-CH_3), 5.11 (1H, s, H-20a), 4.80 (1H, t, *J* = 1.4 Hz, H-20b), 2.13 (3H, s, 2-$OCOCH_3$), 2.06 (3H, s, 10-$OCOCH_3$); ^{13}C-NMR (125 MHz, $CDCl_3$) *δ*: 48.7 (C-1), 70.1 (C-2), 40.9 (C-3), 147.5 (C-4), 76.4 (C-5), 30.6 (C-6), 25.2 (C-7), 45.0 (C-8), 75.8 (C-9), 76.6 (C-10), 150.2 (C-11), 138.3 (C-12), 199.7 (C-13), 36.1 (C-14), 37.9 (C-15), 37.0 (C-16), 25.6 (C-17), 14.0 (C-18), 17.5 (C-19), 113.6 (C-20), 21.2 (2-$OCOCH_3$), 21.4 (10-$OCOCH_3$), 170.2 (2-$OCOCH_3$), 169.6 (10-$OCOCH_3$)。以上数据与文献报道一致[6]，故鉴定化合物 **7** 为 9-去乙酰基紫杉宁 A。

化合物 **8**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) *δ*: 2.36 (1H, brd, *J* = 11.0 Hz, H-1), 5.49 (1H, dd, *J* = 9.5, 2.0 Hz, H-2), 3.52 (1H, d, *J* = 9.5 Hz, H-3), 4.34 (1H, t, *J* = 2.8 Hz, H-5), 2.14 (1H, m, H-6α), 1.60 (1H, m, H-6β), 5.36 (1H, dd, *J* = 10.5, 5.0 Hz, H-7), 4.91 (1H, d, *J* = 3.5 Hz, H-9), 5.35 (1H, d, *J* = 3.5 Hz, H-10), 2.64 (1H, d, *J* = 18.5 Hz, H-14α), 3.02 (1H, dd, *J* = 18.5, 11.5 Hz, H-14β), 4.15 (1H, d, *J* = 8.0 Hz, H-16α), 3.67 (1H, d, *J* = 8.0 Hz, H-16β), 5.25 (1H, brs, H-20a), 4.45 (1H, brs, H-20b), 4.07 (1H, s, 11-OH), 2.08 (3H, s, 2-OAc), 2.07 (3H, s, 7-OAc), 2.01 (3H, s, 9-OAc), 1.94 (3H, s, 10-OAc), 1.50 (3H, s, H-17), 1.14 (3H, s, H-18), 1.03 (3H, s, H-19); ^{13}C-NMR (125 MHz, $CDCl_3$) *δ*: 49.3 (C-1), 68.7 (C-2), 38.2 (C-3), 144.3 (C-4), 73.2 (C-5), 39.4 (C-6), 68.2 (C-7), 46.7 (C-8), 75.9 (C-9), 63.9 (C-10),

80.3 (C-11), 91.8 (C-12), 205.4 (C-13), 34.9 (C-14), 49.7 (C-15), 82.0 (C-16), 15.6 (C-17), 11.8 (C-18), 13.5 (C-19), 113.1 (C-20), 20.5 (2, 7-$OCOCH_3$), 21.2 (9-$OCOCH_3$), 21.3 (10-$OCOCH_3$), 168.4 (10-$OCOCH_3$), 172.3 (2-$OCOCH_3$), 169.8 (9-$OCOCH_3$), 168.4 (10-$OCOCH_3$)。以上数据与文献对照一致[10]，故鉴定化合物 **8** 为 5α-去桂皮酰基紫杉欧吉酚。

化合物 **9**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 5.33 (1H, d, J = 3.3 Hz, H-2), 3.07 (1H, d, J = 3.3 Hz, H-3), 4.20 (1H, t, J = 2.8 Hz, H-5), 2.04 (1H, m, H-6a), 1.89 (1H, m, H-6b), 4.26 (1H, dd, J = 11.4, 4.3 Hz, H-7), 4.60 (1H, d, J = 10.6 Hz, H-9), 6.02 (1H, d, J = 10.6 Hz, H-10), 6.05 (1H, m, H-13), 2.50 (1H, dd, J = 15.2, 10.0 Hz, H-14a), 1.87 (1H, m, H-14b), 1.23 (3H, s, 16-CH_3), 1.52 (3H, s, 17-CH_3), 2.15 (3H, s, 18-CH_3), 1.39 (3H, s, 19-CH_3), 3.47 (1H, d, J = 5.3 Hz, H-20a), 2.32 (1H, d, J = 5.3 Hz, H-20b), 2.18 (3H, s, 13-$OCOCH_3$), 2.13 (3H, s, 2-$OCOCH_3$), 2.09 (3H, s, 9-$OCOCH_3$), 2.04 (3H, s, 10-$OCOCH_3$)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 75.9 (C-1), 72.5 (C-2), 40.1 (C-3), 58.3 (C-4), 78.0 (C-5), 32.9 (C-6), 69.5 (C-7), 46.5 (C-8), 78.3 (C-9), 74.0 (C-10), 136.1 (C-11), 140.3 (C-12), 71.0 (C-13), 38.4 (C-14), 43.3 (C-15), 28.3 (C-16), 21.9 (C-17), 15.3 (C-18), 13.4 (C-19), 49.8 (C-20), 20.8 (10-$OCOCH_3$), 21.1 (2-$OCOCH_3$), 21.2 (9-$OCOCH_3$), 21.6 (13-$OCOCH_3$), 168.8～171.2 (2, 9, 10, 13-$OCOCH_3$)。以上数据与文献报道一致[11]，故鉴定化合物 **9** 为 2α, 5α, 10β, 13α-四乙酰基-1β, 7β, 9α-三羟基-4, 20-环氧紫杉烷-11-烯。

化合物 **10**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.94 (1H, m, H-1), 4.19 (1H, brd, J = 5.3 Hz, H-2), 3.15 (1H, d, J = 5.3 Hz, H-3), 4.31 (1H, m, H-5), 1.98 (1H, m, H-6a), 1.64 (1H, m, H-6b), 5.50 (1H, m, H-7), 5.71 (1H, d, J = 10.8 Hz, H-9), 6.10 (1H, d, J = 10.8 Hz, H-10), 4.34 (1H, m, H-13), 2.72 (1H, dd, J = 16.0, 9.3 Hz, H-14a), 1.33 (1H, dd, J = 16.0, 4.6 Hz, H-14b), 0.93 (3H, s, H-16), 1.57 (3H, s, H-17), 2.26 (3H, s, H-18), 0.97 (3H, s, H-19), 5.47 (1H, brs, H-20a), 5.30 (1H, brs, H-20b), 2.04 (3H, s, $OCOCH_3$), 2.01 (3H, s, $OCOCH_3$), 1.96 (3H, s, $OCOCH_3$)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 50.8 (C-1), 68.6 (C-2), 42.3 (C-3), 144.0 (C-4), 75.0 (C-5), 38.3 (C-6), 70.1 (C-7), 47.7 (C-8), 75.8 (C-9), 72.2 (C-10), 132.8 (C-11), 142.2 (C-12), 68.0 (C-13), 32.0 (C-14), 36.9 (C-15), 32.4 (C-16), 26.0 (C-17), 16.9 (C-18), 13.0 (C-19), 117.5 (C-20), 20.6, 21.9, 21.3 ($OCOCH_3$×3), 167.2, 169.7, 168.5 (7, 9, 10-$OCOCH_3$)。以上数据与文献对照一致[12]，故鉴定化合物 **10** 为 7β, 9α, 10β-三乙酰基-2α, 5α, 13α-三羟基紫杉烷-4(20), 11-二烯。

化合物 **11**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.06 (1H, d, J = 7.4 Hz, H-2), 3.01 (1H, d, J = 7.4 Hz, H-3), 4.88 (1H, d, J = 8.5 Hz, H-5), 2.57 (1H, m, H-6a), 1.84 (1H, m, H-6b), 4.21 (1H, t, J = 8.4 Hz, H-7), 4.69 (1H, s, OH-7), 4.32 (1H, dd, J = 9.9, 3.6 Hz, H-9), 4.75 (1H, d, J = 3.6 Hz, 9-OH), 4.55 (1H, dd, J = 9.9, 4.4 Hz, H-10), 4.11 (1H, d, J = 4.4 Hz, 10-OH), 4.58 (1H, m, H-13), 2.25 (1H, dd, J = 14.7, 7.4 Hz, H-14a), 1.76 (1H, dd, J = 14.7, 6.7 Hz, H-14b), 3.63 (1H, s, 15-OH), 1.05 (3H, s, H-16), 1.10 (3H, s, H-17), 1.94 (3H, s, H-18), 1.86 (3H, s, H-19), 4.44 (1H, d, J = 7.8 Hz, H-20a), 4.08 (1H, d, J = 7.8 Hz, H-20b), 2.20 (3H, s, $OCOCH_3$), 8.00 (2H, d, J = 7.3 Hz, Bz-H-2′, 6′), 7.45 (2H, t, J = 8.1 Hz, Bz-H-3′, 5′), 7.59 (1H, t, J = 7.2 Hz, Bz-H-4′)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 67.6 (C-1), 68.6 (C-2), 44.5 (C-3), 80.4 (C-4), 84.9 (C-5), 37.2 (C-6), 72.3 (C-7), 42.6 (C-8), 80.6 (C-9), 68.6 (C-10), 137.3 (C-11), 146.8 (C-12), 77.6 (C-13), 39.7 (C-14), 76.5 (C-15), 27.7 (C-16), 24.9 (C-17), 11.3 (C-18), 12.2 (C-19), 74.7 (C-20), 22.4 (4-$OCOCH_3$), 171.0 (4-$OCOCH_3$), 166.1 (Ar-CO), 129.9 (C-1′), 129.6 (C-2′, 6′), 128.6 (C-3′, 5′), 133.5 (C-4′)。以上数据与文献报道一致[13]，故鉴定化合物 **11** 为 7, 9, 10, 13-tetra-*O*-deacetylabeobaccatin VI。

化合物 **12**：白色粉末状固体（丙酮）。^{1}H-NMR (500 MHz, $CDCl_3$) δ: 5.88 (1H, brs, H-2), 3.07 (1H, d, J = 7.6 Hz, H-3), 4.90 (1H, d, J = 8.1 Hz, H-5), 2.49 (1H, m, H-6a), 1.84 (1H, m, H-6b), 5.36 (1H, t, J = 7.3 Hz, H-7), 5.72 (1H, brd, J = 10.0 Hz, H-9), 4.55 (1H, d, J = 10.0 Hz, H-10), 3.50 (1H, brs, 10-OH), 4.48 (1H, m, H-13), 1.70 (1H, brs, 13-OH), 2.12 (1H, m, H-14a), 1.48 (1H, dd, J = 14.9, 7.2 Hz, H-14b), 1.03 (3H, s, H-16), 1.20 (3H, s, H-17), 1.92 (3H, s, H-18), 1.63 (3H, s, H-19), 4.48 (1H, d, J = 6.9 Hz, H-20a),

4.38 (1H, d, J = 6.9 Hz, H-20b), 2.00～2.14 (各 3H, s, 2, 4, 7, 9-OCOCH_3)；^{13}C-NMR (125 MHz, $CDCl_3$) δ: 66.7 (C-1), 68.1 (C-2), 43.8 (C-3), 79.8 (C-4), 84.9 (C-5), 34.7 (C-6), 70.1 (C-7), 43.3 (C-8), 79.2 (C-9), 66.5 (C-10), 138.6 (C-11), 145.4 (C-12), 77.5 (C-13), 39.5 (C-14), 76.7 (C-15), 27.6 (C-16), 25.9 (C-17), 11.0 (C-18), 12.9 (C-19), 74.8 (C-20), 21.2～22.2 (2, 4, 7, 9-OCOCH_3)。以上数据与文献报道一致[14]，故鉴定化合物 **12** 为 taxacustin。

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