# 苦皮藤种子的化学成分分析

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［摘要］ **目的**：采用现代分离手段和波谱技术研究苦皮藤 *Celastrus angulatus* 种子中的化学成分，为苦皮藤种子物质基础研究和开发利用提供进一步的实验数据。**方法**：将干燥苦皮藤种子石油醚回流提取 3 次，其提取物用 90% 的甲醇-水萃取 3 次；甲醇层经硅胶柱色谱，以石油醚-乙酸乙酯溶剂体系（10∶1～2∶8）梯度洗脱，将各份洗脱液减压蒸干；采用高效液相制备色谱（甲醇-水体系）进一步分离纯化，结合重结晶法，得到纯化合物，并通过理化常数测定和光谱分析鉴定其化学结构，联合应用 1D 和 2D NMR 技术对化合物结构进行归属指认。**结果**：从苦皮藤种子分离得到 6 个 β-二氢沉香呋喃多醇酯类化合物，通过 $^{1}$H-NMR，$^{13}$C-NMR，DEPT，HSQC，HMBC，$^{1}$H-$^{1}$H COSY，NOESY 等 1D，2D NMR 技术对其所有 NMR 信号进行了详细解析和全归属，详细补充了文献数据尤其是 $^{1}$H-NMR 归属数据，其结构分别确证为 1β，15-diacetoxy-8β，9β-dibenzoyloxy-β-dihydroagarofuran（**1**），angulatueoid H（**2**），苦皮种素Ⅱ（**3**），苦皮种素Ⅲ（**4**），1β，15-diacetoxy-8α-hydroxy-9β-benzoyloxy-β-dihydro-agarofuran（**5**），1β，2β，8α-triacetoxy-9β-benzoyloxy-β-15-nicotinoyloxy-β-dihydroagarofuran（**6**）。**结论**：化合物 **1**，**3**，**5** 为首次从苦皮藤中分离得到；化合物 **4** 为首次从自然界中分离得到。

［关键词］ 苦皮藤种子；化学成分；倍半萜
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## Chemical Components from Seeds of *Celastrus angulatus*

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［**Abstract**］ **Objective**: To study on chemical constituents from the seeds of *Celastrus angulatus* by means of modern separation method and spectrum technology, and provide experimental data for its research, development and utilization. **Method**: Dry seeds of *C. angulatus* were extracted by petroleum ether for 3 times. Its extracts were then further extracted by 90% methanol solution for 3 times. From the methanol layer, the compounds were isolated by silica gel column chromatography and petroleum ether-ethyl acetate solvent system (10∶1-2∶8) was used for gradient elution. The eluent received decompressed drying and was further separated and purified by preparative HPLC with methanol-$H_2O$ solvent system, and finally purified by recrystallization. The compounds were identified on the basis of physic-chemical constants and spectral analysis. **Result**: Six compounds were obtained and identified as 1β, 15-diacetoxy-8β, 9β-dibenzoyloxy-β-dihydroagarofuran (**1**), angulatueoid H (**2**), angulatinoid Ⅱ (**3**), angulatinoid Ⅲ (**4**), 1β, 15-diacetoxy-8α-hydroxy-9β-benzoyloxy-β-dihydroagarofuran (**5**) and 1β, 2β, 8α-triacetoxy-9β-benzoyloxy-β-15-nicotinoyloxy-β-dihydroagarofuran (**6**) respectively, with their NMR data

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detected through 1D ($^1$H, $^{13}$C-NMR and DEPT) and 2D NMR ($^1$H-$^1$H COSY, HSQC, HMBC and NOESY) techniques. **Conclusion**: Compounds **1**, **3** and **5** were obtained from *C. angulatus* for the first time. Compound **4** was obtained from the nature for the first time.

[**Key words**] *Celastrus angulatus*; chemical constituents; sesquiterpenes

苦皮藤分布在河北、山东、河南、陕西、湖北、甘肃、江苏、安徽等省[1]。其根、茎、叶、果实和种子是天然的杀虫剂又是重要的中药资源,民间用其根皮、茎皮、树叶防治蔬菜及各种作物的虫害已有相当长的历史[2]。苦皮藤一直是南蛇藤属植物的研究重点和热点,近年来,由于其抗肿瘤促进和神经保护活性以及在自身免疫性疾病中的应用,在中医中使用的南蛇藤属物种苦皮藤已经引起了更多的关注[3-4]。研究证明苦皮藤主要活性成分为倍半萜化合物,以及生物碱、三萜类、二萜、黄酮类化合物;其中,具有杀虫活性、抗癌活性、神经保护活性等作用的$\beta$-二氢沉香呋喃多元醇酯类物质及其生物碱为苦皮藤成分研究的重点和热点[3-7]。为了阐明其药效物质基础,本课题组采用现代分离手段和波谱技术对苦皮藤进行了系统的化学成分研究。在笔者前期的研究中,从苦皮藤根皮及其叶中分离得到 16 个新的$\beta$-二氢沉香呋喃倍半萜多醇酯类化合物及其生物碱,其中一些新化合物被发现具有抗肿瘤活性[8-19]。在此基础上,为了进一步研究苦皮藤种子的化学成分,从其石油醚提取物 90% 甲醇萃取物中分离得到 6 个$\beta$-二氢沉香呋喃多醇酯类化合物,通过$^1$H-NMR, $^{13}$C-NMR, DEPT, HSQC, HMBC, $^1$H-$^1$H COSY, NOESY 等 1D, 2D NMR 技术对其所有 NMR 信号进行了详细解析和全归属,详细补充了文献数据,特别是$^1$H-NMR 归属数据,分别鉴定为 1$\beta$,15-diacetoxy-8$\beta$,9$\beta$-dibenzoyloxy-$\beta$-dihydroagarofuran (**1**), angulatueoid H (**2**), 苦皮种素Ⅱ (angulatinoid Ⅱ, **3**), 苦皮种素Ⅲ (angulatinoid Ⅲ, **4**), 1$\beta$, 15-diacetoxy-8$\alpha$-hydroxy-9$\beta$-benzoyloxy-$\beta$-dihydroagarofuran (**5**), 1$\beta$, 2$\beta$, 8$\alpha$-triacetoxy-9$\beta$-benzoyloxy-$\beta$-15-nicotinoyloxy-$\beta$-dihydroagarofuran(**6**)。其中,化合物 **1**,**3**,**5** 为首次从苦皮藤中分离得到;化合物 **4** 为首次从自然界中分离得到。

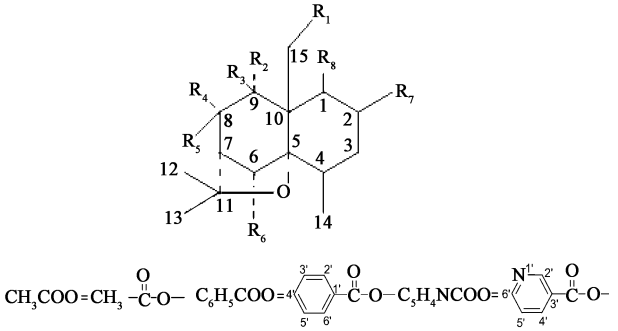
## 1 材料

核磁共振光谱用 ARX-400 型核磁共振仪测定(TMS 内标,瑞士 Bruker 公司);ESI-MS 谱用 Q-Tof Micro™型质谱仪(美国 Waters Micromass 公司);薄层色谱及柱色谱用硅胶(青岛海洋化工厂);所用试剂均为分析纯。

药材采自湖北省,由河南农业大学朱长山教授鉴定为卫矛科南蛇藤属多年生藤状灌木植物苦皮藤 *Celastrus angulatus* 的种子。

## 2 提取与分离

取干燥苦皮藤种子 5 kg,用石油醚回流提取 3 次,合并提取液,减压浓缩得浸膏,将浸膏混悬于适量的水中,用 90% 甲醇溶液萃取 3 次。甲醇层经硅胶柱色谱,以石油醚-乙酸乙酯溶剂体系(10∶1 ~ 2∶8)梯度洗脱,每 500 mL 收集为 1 份,并将各份洗脱液减压蒸干。经高效液相分析后,将成分基本相同的流分合并,并采用高效液相制备色谱进行进一步纯化,结合重结晶法得到化合物。第 60,61 份以甲醇-水(7∶3)溶液作为流动相,经过 HPLC 制备纯化后得到 **1**(15 mg)和 **2**(18 mg);第 208 ~ 209 份以甲醇-水(7∶3)溶液作为流动相,经过 HPLC 制备纯化后得到 **3**(25 mg),第 215 ~ 225 份以甲醇-水(75∶25)溶液作为流动相,经过 HPLC 制备纯化后得到 **4**(20 mg)和 **5**(15 mg);第 325 ~ 330 份以甲醇-水(75∶25)溶液作为流动相,经过 HPLC 制备纯化后得到 **6**(30 mg)。见图 1(结构式及编号统一参照文献[5,8-19])。



**1** $R_1=R_8=CH_3COO$, $R_2=R_4=R_6=R_7=H$, $R_3=R_5=C_6H_5COO$

**2** $R_1=R_2=R_4=R_7=H$, $R_3=R_5=C_6H_5COO$, $R_6=R_8=CH_3COO$

**3** $R_1=R_4=R_7=R_8=CH_3COO$, $R_2=C_6H_5COO$, $R_3=R_5=R_6=H$

**4** $R_1=R_5=R_7=R_8=CH_3COO$, $R_2=R_4=R_6=H$, $R_3=C_6H_5COO$

**5** $R_1=R_8=CH_3COO$, $R_2=R_5=R_6=R_7=H$, $R_3=C_6H_5COO$, $R_4=OH$

**6** $R_1=C_5H_4NCOO$, $R_2=R_5=R_6=H$, $R_3=C_6H_5COO$, $R_4=R_7=R_8=CH_3COO$

**图 1 化合物 1 ~ 6 的化学结构**

**Fig. 1 Structure of compound 1-6**

## 3 结构鉴定

化合物 **1** 白色无定形粉末。ESI-MS (*m/z*) 601 [M + Na]$^+$。$^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 5.40 (1H, dd, *J* = 12.0, 4.6 Hz, H-1), 1.71 (1H, m, H-2a), 1.86 (1H, m, H-2b), 1.50 (1H, m, H-3a), 2.28 (1H, m, H-3b), 1.87 (1H, m, H-4), 1.98 (1H, m, H-6a), 2.80 (1H, m, H-6b), 2.51 (1H, t, *J* = 3.6, 3.6 Hz, H-7), 5.70 (1H, dd, *J* = 5.0, 3.6 Hz, H-8), 5.82 (1H, d, *J* = 5.0 Hz, H-9), 1.26 (3H, s, H-12), 1.61 (3H, s, H-13), 1.16 (3H, d, *J* = 7.8 Hz, H-14), 5.04 (1H, d, *J* = 12.9 Hz, H-15a), 4.86 (1H, d, *J* = 12.9 Hz, H-15b); 1.44 [3H, s, $CH_3$COO-1 ($CH_3$)], 2.00 [3H, s, $CH_3$COO-15 ($CH_3$)]; 8.00 [2H, m, $C_6H_5$COO-8 (2′, 6′)], 7.44 [2H, m, $C_6H_5$COO-8 (3′, 5′)], 7.58 [1H, m, $C_6H_5$COO-8 (4′)]; 7.96 [2H, m, $C_6H_5$COO-9 (2′, 6′)], 7.33 [2H, m, $C_6H_5$COO-9 (3′, 5′)], 7.48 [1H, m, $C_6H_5$COO-9 (4′)]。$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 78.96 (C-1), 23.63 (C-2), 26.80 (C-3), 40.00 (C-4), 88.67 (C-5), 31.96 (C-6), 47.91 (C-7), 71.46 (C-8), 74.87 (C-9), 49.78 (C-10), 80.85 (C-11), 29.94 (C-12), 22.90 (C-13), 16.06 (C-14), 61.88 (C-15); $CH_3$COO-1: 170.13 (C = O), 20.83 ($CH_3$); $CH_3$COO-15: 170.74 (C = O), 21.46 ($CH_3$); $C_6H_5$COO-8: 165.85 (C = O), 130.24 (C-1′), 129.65 * (C-2′, 6′), 128.68 (C-3′, 5′), 133.17 (C-4′); $C_6H_5$COO-9: 164.96 (C = O), 130.06 (C-1′), 129.57 * (C-2′, 6′), 128.49 (C-3′, 5′), 133.08 (C-4′)。(其中 * 归属可互换)(结构式及编号见图 1)。以上数据与文献[20]报道一致,故鉴定该化合物为 1$\beta$, 15-diacetoxy-8$\beta$, 9$\beta$-dibenzoyloxy-$\beta$-dihydroagarofuran。

化合物 **2** 白色无定形粉末。ESI-MS (*m/z*) 633 [M + Na]$^+$。$^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 5.26 (1H, dd, *J* = 11.4, 4.6 Hz, H-1), 1.58 (1H, m, H-2a), 1.68 (1H, m, H-2b), 1.45 (1H, m, H-3a), 2.15 (1H, m, H-3b), 2.26 (1H, m, H-4), 6.19 (1H, br s, H-6), 2.58 (1H, br d, *J* = 4.4 Hz, H-7), 5.82 (1H, dd, *J* = 5.3, 4.4 Hz, H-8), 5.67 (1H, d, *J* = 5.3 Hz, H-9), 1.46 (3H, s, H-12), 1.63 (3H, s, H-13), 1.08 (3H, d, *J* = 7.4 Hz, H-14), 1.53 (3H, s, H-15); 1.42 [3H, s, $CH_3$COO-1 ($CH_3$)], 2.13 [3H, s, $CH_3$COO-6 ($CH_3$)]; 8.05 [2H, m, $C_6H_5$COO-8 (2′, 6′)], 7.47 [2H, m, $C_6H_5$COO-8 (3′, 5′)], 7.57 [1H, m, $C_6H_5$COO-8 (4′)]; 7.89 [2H, m, $C_6H_5$COO-9 (2′, 6′)], 7.32 [2H, m, $C_6H_5$COO-9 (3′, 5′)], 7.49 [1H, m, $C_6H_5$COO-9 (4′)]。$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 78.88 (C-1), 22.11 (C-2), 26.56 (C-3), 33.82 (C-4), 91.04 (C-5), 74.99 (C-6), 52.88 (C-7), 71.70 (C-8), 74.48 (C-9), 48.73 (C-10), 81.70 (C-11), 30.62 (C-12), 24.25 (C-13), 16.85 (C-14), 12.32 (C-15); $CH_3$COO-1: 170.23 (C = O), 20.87 ($CH_3$); $CH_3$COO-6: 170.04 (C = O), 21.34 ($CH_3$); $C_6H_5$COO-8: 165.48 (C = O), 130.00 * (C-1′), 129.74 (C-2′, 6′), 128.55 (C-3′, 5′), 133.12 (C-4′); $C_6H_5$COO-9: 165.02 (C = O), 129.86 * (C-1′), 129.56 (C-2′, 6′), 128.34 (C-3′, 5′), 133.03 (C-4′)。(其中 * 归属可互换)(结构式及编号见图 1)。以上数据与文献[21]报道一致,故鉴定该化合物为 angulatueoid H。

化合物 **3** 白色无定形粉末。ESI-MS (*m/z*) 597 [M + Na]$^+$。$^1$H-NMR (600 MHz, $CDCl_3$) $\delta_H$: 5.68 (1H, d, *J* = 3.2 Hz, H-1), 5.56 (1H, m, H-2), 1.80 (1H, dd, *J* = 15.3, 2.2 Hz, H-3a), 2.48 (1H, ddd, *J* = 15.3, 6.8, 2.2 Hz, H-3b), 2.01 (1H, m, H-4), 2.30 (1H, d, *J* = 11.9 Hz, H-6a), 2.40 (1H, d, *J* = 11.9 Hz, H-6b), 2.32 (1H, d, *J* = 3.0 Hz, H-7), 5.69 (1H, dd, *J* = 6.2, 3.0 Hz, H-8), 5.60 (1H, d, *J* = 6.2 Hz, H-9), 1.25 (3H, s, H-12), 1.55 (3H, s, H-13), 1.30 (3H, d, *J* = 8.1 Hz, H-14), 4.53 (1H, d, *J* = 12.7 Hz, H-15a), 4.74 (1H, d, *J* = 12.7 Hz, H-15b); 1.65 [3H, s, $CH_3$COO-1 ($CH_3$)], 1.91 * [3H, s, $CH_3$COO-2 ($CH_3$)], 2.11 * [3H, s, $CH_3$COO-8 ($CH_3$)], 2.29 [3H, s, $CH_3$COO-15 ($CH_3$)]; 8.09 [2H, m, $C_6H_5$COO-9 (2′, 6′)], 7.48 [2H, m, $C_6H_5$COO-9 (3′, 5′)], 7.60 [1H, m, $C_6H_5$COO-9 (4′)]。$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 71.08 (C-1), 69.80 (C-2), 30.89 (C-3), 39.10 (C-4), 86.09 (C-5), 36.39 (C-6), 48.24 (C-7), 71.72 (C-8), 68.60 (C-9), 51.53 (C-10), 82.34 (C-11), 31.00 (C-12), 25.04 (C-13), 18.82 (C-14), 64.42 (C-15); $CH_3$COO-1: 169.39 (C = O), 20.33 (-$CH_3$); $CH_3$COO-2: 169.96 (C = O), 20.88 * * ($CH_3$); $CH_3$COO-8: 169.96 (C = O), 21.34 * * ($CH_3$); $CH_3$COO-15: 170.55 (C = O), 21.41 ($CH_3$); $C_6H_5$COO-9: 165.79 (C = O), 129.17 (C-1′), 130.27 (C-2′, 6′), 128.29 (C-3′, 5′), 133.38 (C-4′)。(其中 *, * * 归属可互换)(结构

式及编号见图 1)。通过 DEPT, NOE, HSQC, HMBC, $^1$H-$^1$H COSY, NOESY 等 1D,2D NMR 技术对其所有 NMR 信号进行详细解析和全归属,鉴定该化合物为苦皮种素Ⅱ(angulatinoid Ⅱ)[22-23]。

化合物 **4** 白色无定形粉末。ESI-MS ($m/z$) 597 [M + Na]$^+$。$^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 5.51 (1H, d, $J$ = 3.3 Hz, H-1), 5.40 (1H, m, H-2), 1.74 (1H, dd, $J$ = 15.2, 3.9 Hz, H-3a), 2.44 (1H, ddd, $J$ = 15.2, 6.6, 3.9 Hz, H-3b), 1.94 (1H, m, H-4), 2.08 (1H, dd, $J$ = 12.9, 3.4 Hz, H-6a), 2.92 (1H, d, $J$ = 12.9 Hz, H-6b), 2.31 (1H, t, $J$ = 3.4, 3.4 Hz, H-7), 5.56 (1H, dd, $J$ = 5.6, 3.4 Hz, H-8), 5.63 (1H, d, $J$ = 5.6 Hz, H-9), 1.23 (3H, s, H-12), 1.53 (3H, s, H-13), 1.31 (3H, d, $J$ = 8.0 Hz, H-14), 4.86 (1H, d, $J$ = 12.7 Hz, H-15a), 5.13 (1H, d, $J$ = 12.7 Hz, H-15b); 1.51 [3H, s, $CH_3$COO-1 ($CH_3$)], 2.03 * [3H, s, $CH_3$COO-2 ($CH_3$)], 2.06 * [3H, s, $CH_3$COO-8 ($CH_3$)], 2.10 [3H, s, $CH_3$COO-15 ($CH_3$)]; 7.99 [2H, m, $C_6H_5$COO-9 (2′,6′)], 7.44 [2H, m, $C_6H_5$COO-9 (3′,5′)], 7.56 [1H, m, $C_6H_5$COO-9 (4′)]。$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 77.17 (C-1), 69.82 (C-2), 31.41 (C-3), 39.26 (C-4), 87.77 (C-5), 32.13 (C-6), 48.23 (C-7), 69.80 (C-8), 73.70 (C-9), 49.32 (C-10), 80.61 (C-11), 29.85 (C-12), 23.07 (C-13), 18.38 (C-14), 61.97 (C-15); $CH_3$COO-1: 169.94 (C = O), 20.52 ($CH_3$); $CH_3$COO-2: 170.01 (C = O), 21.34 * ($CH_3$); $CH_3$COO-8: 169.96 (C = O), 21.11 * ($CH_3$); $CH_3$COO-15: 170.55 (C = O), 21.58 ($CH_3$); $C_6H_5$COO-9: 164.86 (C = O), 129.64 (C-1′), 129.54 (C-2′, 6′), 128.53 (C-3′, 5′), 133.27 (C-4′)。(其中 * 归属可互换)(结构式及编号见图 1)。通过 DEPT, NOE, HSQC, HMBC, $^1$H-$^1$H COSY, NOESY 等 1D,2D NMR 技术对其所有 NMR 信号进行详细解析和全归属,鉴定该化合物为苦皮种素Ⅲ(angulatinoid Ⅲ)[22]。

化合物 **5** 白色无定形粉末。ESI-MS ($m/z$) 497 [M + Na]$^+$。$^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 5.36 (1H, dd, $J$ = 11.8, 4.3 Hz, H-1), 1.50 (1H, m, H-2a), 1.74 (1H, m, H-2b), 1.45 (1H, m, H-3a), 2.19 (1H, m, H-3b), 1.82 (1H, q, $J$ = 7.8 Hz, H-4), 2.02 (1H, dd, $J$ = 12.6, 5.1 Hz, H-6a), 2.60 (1H, d, $J$ = 12.6 Hz, H-6b), 2.35 (1H, dd, $J$ = 5.1, 3.1 Hz, H-7), 4.24 (1H, dd, $J$ = 9.3, 3.1 Hz, H-8), 5.80 (1H, d, $J$ = 9.3 Hz, H-9), 1.22 (3H, s, H-12), 1.57 (3H, s, H-13), 1.12 (3H, d, $J$ = 7.8 Hz, H-14), 4.47 (1H, d, $J$ = 12.6 Hz, H-15a), 4.95 (1H, d, $J$ = 12.6 Hz, H-15b); 1.43 [3H, s, $CH_3$COO-1 ($CH_3$)], 2.20 [3H, s, $CH_3$COO-15 ($CH_3$)]; 8.01 [2H, m, $C_6H_5$COO-9 (2′, 6′)], 7.45 [2H, m, $C_6H_5$COO-9 (3′, 5′)], 7.57 [1H, m, $C_6H_5$COO-9 (4′)], 2.55 [1H, br, OH-8]。$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 78.45 (C-1), 23.00 (C-2), 26.52 (C-3), 39.86 (C-4), 88.29 (C-5), 36.26 (C-6), 49.10 (C-7), 75.85 (C-8), 80.47 (C-9), 50.03 (C-10), 81.74 (C-11), 31.10 (C-12), 24.81 (C-13), 16.89 (C-14), 61.74 (C-15); $CH_3$COO-1: 170.08 (C = O), 20.82 ($CH_3$); $CH_3$COO-15: 170.48 (C = O), 21.51 ($CH_3$); $C_6H_5$COO-9: 167.55 (C = O), 129.81 (C-1′), 129.75 (C-2′, 6′), 128.64 (C-3′, 5′), 133.43 (C-4′)。(结构式及编号见图 1)。与文献[20]报道一致,故鉴定该化合物为 1$\beta$,15-diacetoxy-8$\alpha$-hydroxy-9$\beta$-benzoyloxy-$\beta$-dihydroagarofuran。

化合物 **6** 白色无定形粉末。ESI-MS ($m/z$) 660 [M + Na]$^+$。$^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 5.59 (1H, d, $J$ = 3.2 Hz, H-1), 5.46 (1H, m, H-2), 1.77 (1H, dd, $J$ = 15.2, 1.9 Hz, H-3a), 2.41 (1H, m, H-3b), 1.96 (1H, q, $J$ = 8.0 Hz, H-4), 2.22 (1H, dd, $J$ = 13.0, 4.8 Hz, H-6a), 2.66 (1H, d, $J$ = 13.0 Hz, H-6b), 2.43 (1H, m, H-7), 5.78 (1H, dd, $J$ = 9.7, 3.3 Hz, H-8), 6.06 (1H, d, $J$ = 9.7 Hz, H-9), 1.23 (3H, s, H-12), 1.57 (3H, s, H-13), 1.35 (3H, d, $J$ = 8.0 Hz, H-14), 4.83 (1H, d, $J$ = 13.1 Hz, H-15a), 5.35 (1H, d, $J$ = 13.1 Hz, H-15b); 1.60 [3H, s, $CH_3$COO-1 ($CH_3$)], 2.10 [3H, s, $CH_3$COO-2 ($CH_3$)], 1.88 [3H, s, $CH_3$COO-8 ($CH_3$)]; 7.83 [2H, m, $C_6H_5$COO-9 (2′, 6′)], 7.32 [2H, m, $C_6H_5$COO-9 (3′, 5′)], 7.48 [1H, m, $C_6H_5$COO-9 (4′)]; 9.46 [1H, br s, $C_5H_4$NCOO-15 (2′)], 8.57 [1H, br d, $J$ = 7.9 Hz, $C_5H_4$NCOO-15 (4′)], 7.54 [1H, dd, $J$ = 7.9, 3.9 Hz, $C_5H_4$NCOO-15 (5′)], 8.87 [1H, d, $J$ = 3.9 Hz, $C_5H_4$NCOO-15 (6′)]。$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 76.31 (C-1), 69.17 (C-2), 31.00 (C-3), 39.14 (C-4), 87.69 (C-5), 36.38 (C-6), 47.21 (C-7), 75.37 (C-8), 76.31 (C-9), 50.58 (C-10), 82.07 (C-11), 30.64 (C-12), 24.47 (C-13), 18.64 (C-14), 63.37 (C-15); $CH_3$COO-1: 169.71 (C = O), 20.61 ($CH_3$); $CH_3$COO-2: 169.83

(C=O), 21.33 ($CH_3$); $CH_3COO$-8: 170.51 (C=O), 20.88 ($CH_3$); $C_6H_5COO$-9: 165.55 (C=O), 129.55 (C-1′), 129.42 (C-2′, 6′), 128.60 (C-3′, 5′), 133.24 (C-4′); $C_5H_4NCOO$-15: 165.35 (C=O), 150.89 (C-2′), 125.75 (C-3′), 137.27 (C-4′), 123.83 (C-5′), 153.68 (C-6′)。(结构式及编号见图 1)。以上数据与文献[24]报道一致,故鉴定该化合物为 1β, 2β, 8α-triacetoxy-9β-benzoyloxy-β-15-nicotinoyloxy-β-dihydroagarofuran。

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