川楝子中的化学成分研究

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[摘要] **目的**:研究黔产川楝子中的化学成分。**方法**:应用正、反相硅胶(RP-18 型)柱层析;葡聚糖凝胶(Sephadex LH-20 型)柱层析,结合重结晶方法进行分离纯化,运用^{1}H-NMR,^{13}C-NMR,ESI-MS 和 ES-MS 等现代波谱技术对化合物的结构进行鉴定。**结果**:从黔产川楝子乙醇提取物中分离鉴定了 12 个化合物,分别被鉴定为:1-*O*-tigloyl-1-*O*-debenzoylohchinal (**1**),印楝醛(ohchinal,**2**),1-cinnamoyltrichilinin (**3**),3, 7-diacetyl-14, 15-deoxyhavanensin (**4**),7-*O*-acetyl-14, 15-deoxyhavanensin (**5**),6α-*O*-acetyl-7-deacetylnimocinol (**6**),6α-hydroxyazadirone (**7**),24-Nor-5ξ-13α, 17α-chola-14, 20, 22-triene-3β, 7α-diol-21, 23-epoxy-4, 4, 8-trimethyl-3-acetate (**8**),hedyotol-A (**9**),2, 6-bis(3-methoxy-4-hydroxyphenyl)-3, 7-dioxabicyclo[3, 3, 0]octan-8-one (**10**),exo-endo-2, 6-bis(4′-hydroxy-3′-methoxy-phenyl)-3, 7-dioxabicyclo[3, 3, 0]octane (**11**)和 betulafolienediolone (**12**)。**结论**:化合物 **2** ~ **12** 均为首次从该植物中分离得到。

[关键词] 川楝子;化学成分;分析纯化;结构鉴定
[中图分类号] R284.1 [文献标识码] A [文章编号] 1005-9903(2013)18-0090-06
[doi] 10.11653/syfj201318090

Study on Chemical Constituents of Fructus *Melia toosendan*

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[**Abstract**] **Objective**: To study the chemical constituents of fructus *Melia toosendan*. **Method**: Normal phase silica gel, RP-18 Silica gel and Sephadex LH-20 column chromatographies combined with recrystallization were used to isolate and purify the constituents. Their structures were identifided by spectroscopic methods, including ^{1}H-NMR, ^{13}C-NMR, ESI-MS and EI-MS. **Result**: Twelve compounds were isolated. Their structures were decided as 1-*O*-tigloyl-1-*O*-debenzoylohchinal (**1**), ohchinal (**2**), 1-cinnamoyltrichilinin (**3**), 3, 7-diacetyl-14, 15-deoxyhavanensin (**4**), 7-*O*-acetyl-14, 15-deoxyhavanensin (**5**), 6α-*O*-acetyl-7-deacetylnimocinol (**6**), 6α-hydroxyazadirone (**7**), 24-nor-5ξ-13α, 17α-chola-14, 20, 22-triene-3β, 7α-diol-21, 23-epoxy-4, 4, 8-trimethyl-3-acetate (**8**), hedyotol-A (**9**), 2, 6-bis (3-methoxy-4-hydroxyphenyl) -3, 7-dioxabicyclo [3, 3, 0] octan-8-one (**10**), exo-endo-2, 6-bis (4′-hydroxy-3′-methoxy-phenyl) -3, 7-dioxabicyclo [3, 3, 0] octane (**11**) and betulafolienediolone (**12**). **Conclusion**: Compounds **2-12** were obtained from fructus *M. toosendan* for the first time.

[**Key words**] fructus *Melia toosendan*; chemical constituents; separation and purification; structural identification

[收稿日期] 20130605(006)
[基金项目] 国家自然科学基金项目(31160374);国家 973 计划支撑项目(2012CB722601)
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川楝是楝科 Meliaceae 楝属 *Melia* 植物。产于甘肃、湖北、四川、贵州和云南等省,其他省区广泛栽培;生于土壤湿润、肥沃的杂木林和疏林内。分布于日本、中南半岛(《中国植物志》编辑委员会,1997)。川楝子是川楝的果实,为川楝的主要药用部位,用药历史悠久,其原名为楝实,首载于《本经》,亦称为金铃子《本草纲目》,以川中者为良。川楝子味苦,性寒,小毒,归肝、胃,小肠经。主要用于疏肝泻火,行气止痛,杀虫。主治脘腹胁肋疼痛,疝气疼痛,虫积腹痛,头癣等[1]。本研究目的在于对川楝子中的化学成分尤其是微量成分进行系统深入研究,从其乙醇提取物中分离鉴定了 12 个化合物,其中 11 个化合物(化合物 **2** ~ **12**)均为首次从该植物中分离得到。本研究为进一步研究川楝子中的生理活性成分提供物质基础和科学依据。

1 材料

熔点测定:双目显微熔点测定仪(XT-4),温度未校正;核磁共振谱测定:核磁共振仪(INOVA-400 型),TMS 为内标,氘代试剂为 J&K CHEMICAL LTD 生产;EI-MS 测定:EI 质谱仪(HP-5973 型);ESI-MS 测定:ESI 质谱仪(HP1100MSD);半制备型高效液相色谱:半制备液相色谱仪(Waters),半制备用色谱柱为 SunFire™-C_{18} (Waters, 10 μm, 10 mm × 150 mm)柱;正相硅胶(40 ~ 80, 200 ~ 300, 300 ~ 400 目),硅胶 H(10 ~ 40 μm)和薄层层析硅胶 GF_{254} (0.20 ~ 0.25 mm),以上硅胶材料均为青岛海洋化工厂出品;反相硅胶材料 RP-18(40 ~ 60 μm)为 Merck 公司出品;柱层析凝胶材料 Sephadex LH-20 (40 ~ 70 μm)为 Amersham Pharmacia Biotech AB (Uppsala, Sweden)公司出品;提取和分离所用的有机溶剂均为工业级,使用前经重蒸处理;高效液相色谱所用溶剂均为色谱级。

实验所选用的供试样品为植物川楝的果实,于 2010 年 4 月购买于贵州省贵阳市三桥药材市场,该植物样品由贵阳市中医学院孙庆文老师鉴定为植物川楝 *Melia toosendan* Sieb. et Zucc. 的干燥成熟果实。

2 提取分离

干燥的川楝子(约 30 kg),经粉碎后用 95% 乙醇加热回流提取 3 次,时间依次为 4,3,3 h。提取液减压浓缩得到总浸膏,加适量水使其混悬,然后依次用石油醚和乙酸乙酯溶剂进行萃取,得到石油醚萃取物(约 625 g),乙酸乙酯萃取物(约 688 g)。将上述乙酸乙酯萃取物,采用正相硅胶柱层析进行粗分段,用氯仿和甲醇混合溶剂梯度洗脱(氯仿-甲醇 100∶0 ~ 0∶100),薄层层析(TLC)进行跟踪检测,合并成分相似部分,将乙酸乙酯萃取部分共分成 9 段(Fr. 1-Fr. 9)。将 Fr. 4 部分通过 RP18 反相硅胶柱层析进行分段处理,析出的晶体通过 Sephadex LH-20(氯仿-甲醇 1∶1)柱层析后,再采用正相硅胶柱层析、RP18 反相硅胶柱层析纯化可得到化合物 **1**(33 mg);Fr. 4-1 段样品通过正相硅胶柱层析得到化合物 **2**(8 mg);余下样品经过反复正相硅胶柱层析和反相硅胶柱层析得到化合物 **3**(8 mg)。将 Fr. 5 段样品经反相硅胶分段后,反复利用正相硅胶柱层析可得到化合物 **4**(10 mg),**5**(8 mg),**6**(16 mg);Fr. 5-1 段样品经半制备 HPLC(流动相为甲醇-水 77∶23)可得到化合物 **7**(32 mg)。Fr. 6 段样品经反复硅胶柱层析和 Sephadex LH-20 柱层析、反相硅胶 RP18 柱层析可得到化合物 **8**(10 mg),**9**(10 mg),**11**(5 mg);Fr. 6-1 段样品采用半制备 HPLC(流动相为甲醇-水 70∶30)得到化合物 **12**(22 mg)。Fr. 7 段样品经反复硅胶柱层析和 Sephadex LH-20 柱层析得到化合物 **10**(55 mg)。

3 结构鉴定

化合物 **1** 白色片状晶体(氯仿),mp 206 ~ 208 ℃;EI-MS: *m/z* 566 $[M]^+$;^{1}H-NMR (400 MHz, $CDCl_3$) δ:4.48(1H, s, H-1), 2.43 ~ 2.39(1H, m, Ha-2), 2.43 ~ 2.39(1H, m, Hb-2), 4.99(1H, s, H-3), 2.79(1H, d, J = 12.4 Hz, H-5), 4.03(1H, t-like, H-6), 4.22(1H, d, J = 12.0 Hz, H-7), 2.65(1H, d, J = 10.4 Hz, H-9), 2.33 ~ 2.22(1H, m, Ha-11), 2.33 ~ 2.22(1H, m, Hb-11), 9.15(1H, d, J = 4.8 Hz, H-12), 5.32(1H, m, H-15), 2.33 ~ 2.22(1H, m, Ha-16), 2.18 ~ 2.13(1H, m, Hb-16), 3.61(1H, d, J = 7.2 Hz, H-17), 1.60(3H, s, H-18), 0.99(3H, s, H-19), 7.14(1H, s, H-21), 6.12(1H, s, H-22), 7.35(1H, s, H-23), 3.65(1H, d, J = 7.6 Hz, Ha-28), 3.71(1H, d, J = 7.2 Hz, Hb-28), 1.23(3H, s, H-29), 1.28(3H, s, H-30), 6.99(1H, s, H-3′), 1.89(3H, s, H-2′), 1.79(3H, s, H-3′), 1.97(3H, s, H-OAc);^{13}C-NMR(100 MHz, $CDCl_3$), δ:71.9(d, C-1), 28.1(t, C-2), 71.2(d, C-3), 42.7(s, C-4), 40.0(d, C-5), 72.6(d, C-6), 85.6(d, C-7), 48.6(s, C-8), 38.2(d, C-9), 40.7(s, C-10), 40.5(t, C-11), 199.4(d, C-12), 136.5(s, C-13), 145.5(s, C-14), 88.0(d, C-15), 41.8(t, C-16), 49.4(d, C-17), 13.5(q, C-18), 15.4(q, C-19), 126.7(s, C-20), 138.3(d, C-21), 109.9

(d, C-22), 143.2 (d, C-23), 77.7 (t, C-28), 19.6 (q, C-29), 16.8 (q, C-30), 166.4 (s, C-1′), 128.6 (s, C-2′), 138.3 (d, C-3′), 14.4 (q, C-2′), 12.0 (q, C-3′), 170.4 (s, $COCH_3$), 21.0 (q, $COCH_3$)。以上数据与参考文献对照分析[2], 可鉴定该化合物为 1-*O*-tigloyl-1-*O*-debenzoylohchinal。

化合物 **2** 白色固体(氯仿), EI-MS: *m/z* 588 $[M]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.06 (1H, d, *J* = 18.8 Hz, H-1), 5.34 (1H, t-like, H-3), 2.95 (1H, d, *J* = 12.4 Hz, H-5), 4.05 (1H, d, *J* = 12.4 Hz, H-6), 4.23 (1H, s, H-7), 2.72 (1H, d, *J* = 10.8 Hz, H-9), 8.90 (1H, d, *J* = 4.8 Hz, H-12), 5.77 (1H, s, H-15), 3.61 (1H, d, *J* = 8.4 Hz, H-17), 1.52 (3H, s, H-18), 1.05 (3H, s, H-19), 7.17 (1H, s, H-21), 7.00 (1H, s, H-22), 7.47 (1H, t, *J* = 7.2 Hz, H-23), 3.65 (1H, d, *J* = 7.2 Hz, Ha-28), 3.80 (1H, d, *J* = 7.6 Hz, Hb-28), 1.27 (3H, s, H-29), 1.27 (3H, s, H-30), 8.15 (1H, d, *J* = 7.6 Hz, H-3′, 7′), 7.47 (1H, t, *J* = 7.2 Hz, H-4′, 6′), 7.61 (1H, t, *J* = 7.2 Hz, H-5′), 1.97 (3H, s, H-OAc); ^{13}C-NMR (100 MHz, $CDCl_3$), δ: 71.9 (d, C-1), 28.0 (t, C-2), 71.1 (d, C-3), 42.6 (s, C-4), 40.0 (d, C-5), 72.6 (d, C-6), 85.6 (d, C-7), 48.4 (s, C-8), 38.1 (d, C-9), 40.7 (s, C-10), 40.5 (t, C-11), 199.1 (d, C-12), 136.8 (s, C-13), 144.9 (s, C-14), 88.0 (d, C-15), 41.6 (t, C-16), 49.4 (d, C-17), 13.3 (q, C-18), 15.2 (q, C-19), 126.4 (s, C-20), 138.2 (d, C-21), 109.5 (d, C-22), 143.1 (d, C-23), 77.6 (t, C-28), 19.5 (q, C-29), 16.7 (q, C-30), 164.9 (s, C-1′), 129.6 (s, C-2′), 129.6 (d, C-3′, 7′), 128.6 (d, C-4′, 6′), 133.6 (d, C-5′), 170.4 (s, $COCH_3$), 20.9 (q, $COCH_3$)。以上数据与参考文献对照分析[2], 可鉴定该化合物为印楝醛(ohchinal)。

化合物 **3** 白色晶体(氯仿), mp 134 ~ 136℃; EI-MS: *m/z* 658 $[M]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 4.72 (1H, t-like, H-1), 4.96 (1H, t-like, H-3), 2.84 (1H, d, *J* = 12.4 Hz, H-5), 4.21 (1H, dd, *J* = 12.4, 2.8 Hz, H-6), 4.26 (1H, d, *J* = 2.4 Hz, H-7), 2.93-2.90 (1H, m, H-9), 5.07 (1H, t, *J* = 8.0 Hz, H-12), 5.72 (1H, d-like, H-15), 3.02-2.99 (1H, m, H-17), 1.05 (3H, s, H-18), 0.97 (3H, s, H-19), 7.17 (1H, s, H-21), 6.19 (1H, s, H-22), 7.40 (1H, d, *J* = 5.2 Hz, H-23), 3.63 (1H, d, *J* = 7.6 Hz, Ha-28), 3.68 (1H, d, *J* = 7.6 Hz, Hb-28), 1.15 (3H, s, H-29), 1.24 (3H, s, H-30), 6.40 (1H, d, *J* = 16.0 Hz, H-2′), 7.75 (1H, d, *J* = 16.0 Hz, H-3′), 7.49-7.47 (2H, d, m, H-5′, 5″), 7.49-7.47 (2H, d, m, H-6′, 6″), 7.40 (1H, d, *J* = 5.2 Hz, H-7′), 1.87 (3H, brs, 3-OAc), 1.87 (3H, brs, 12-OAc); ^{13}C-NMR (100 MHz, $CDCl_3$), δ: 72.5 (d, C-1), 27.2 (t, C-2), 71.6 (d, C-3), 42.2 (s, C-4), 39.5 (d, C-5), 72.1 (d, C-6), 73.8 (d, C-7), 45.3 (s, C-8), 34.3 (d, C-9), 39.3 (s, C-10), 24.1 (t, C-11), 77.1 (d, C-12), 51.4 (s, C-13), 157.2 (s, C-14), 122.8 (d, C-15), 36.6 (t, C-16), 50.2 (d, C-17), 26.8 (q, C-18), 15.2 (q, C-19), 124.3 (s, C-20), 140.1 (d, C-21), 111.6 (d, C-22), 142.0 (d, C-23), 77.9 (t, C-28), 19.5 (q, C-29), 15.4 (q, C-30), 165.5 (s, C-1′), 117.8 (d, C-2′), 145.5 (d, C-3′), 133.9 (s, C-4′), 128.0 (d, C-5′, 5″), 129.0 (d, 6′, 6″), 130.6 (d, C-7′), 170.2 (s, 3-$COCH_3$), 21.1 (q, 3-$COCH_3$), 170.9 (s, 12-$COCH_3$), 21.3 (q, 12-$COCH_3$)。以上数据与参考文献对照分析[3], 可鉴定该化合物为 1-cinnamoyltrichilinin。

化合物 **4** 无色固体(甲醇); EI-MS: *m/z* 498 $[M]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 3.52 (1H, t-like, H-1), 4.96 (1H, t, *J* = 2.8 Hz, H-3), 1.90-1.79 (1H, m, H-5), 5.24 (1H, t, *J* = 2.8 Hz, H-7), 2.71 (1H, dd, *J* = 11.6, 7.2 Hz, H-9), 5.35 (1H, d, *J* = 2.0 Hz, H-15), 2.80 (1H, dd, *J* = 10.8, 7.6 Hz, H-17), 0.86 (3H, s, H-18), 0.94 (3H, s, H-19), 7.26 (1H, s, H-21), 6.30 (1H, d, *J* = 0.8 Hz, H-22), 7.39 (1H, t, *J* = 1.6 Hz, H-23), 0.95 (3H, s, H-28), 0.82 (3H, s, H-29), 1.18 (3H, s, H-30), 2.01 (3H, s, 1-OAc), 2.13 (3H, s, 3-OAc); ^{13}C-NMR (100 MHz, $CDCl_3$), δ: 71.2 (d, C-1), 28.3 (t, C-2), 78.7 (d, C-3), 36.2 (s, C-4), 36.4 (d, C-5), 23.0 (t, C-6), 75.0 (d, C-7), 42.0 (s, C-8), 35.6 (d, C-9), 46.1 (s, C-10), 15.7 (t, C-11), 32.9 (t, C-12), 47.3 (s, C-13), 159.9 (s, C-14), 118.2 (d, C-15), 34.3 (t, C-16), 51.4 (d, C-17), 19.9 (q, C-18), 16.3 (q, C-19), 124.9 (s, C-20), 139.6 (d, C-21), 111.1 (d, C-22), 142.4 (d, C-23), 27.3 (q, C-28), 21.4 (q, C-29), 27.5 (q, C-30), 170.3 (s, 1-$COCH_3$), 21.3 (q, 1-$COCH_3$), 169.5 (s, 3-$COCH_3$), 21.3 (q, 3-$COCH_3$)。以上数据与参考文献对照分析[4], 可鉴定该化合物为 3, 7-diacetyl-14, 15-deoxyhavanensin。

化合物 **5** 无色固体(甲醇); EI-MS: *m/z* 456 $[M]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 3.58 (1H, t-

like,H-1),3.55(1H,t-like,H-3),2.25-2.14(1H,m,H-5),5.22(1H,t-like,H-7),2.71(1H,dd,J=11.2,7.2 Hz,H-9),5.33(1H,d,J=1.6 Hz,H-15),2.78(1H,dd,J=10.8,7.6 Hz,H-17),0.83(3H,s,H-18),0.92(3H,s,H-19),7.24(1H,s,H-21),6.29(1H,brs,H-22),7.38(1H,t,J=1.6 Hz,H-23),0.92(3H,s,H-28),0.85(3H,s,H-29),1.17(3H,s,H-30),2.00(3H,s,3-OAc);^{13}C-NMR(100 MHz,$CDCl_3$),δ:72.3(d,C-1),29.5(t,C-2),77.8(d,C-3),37.2(s,C-4),35.5(d,C-5),23.1(t,C-6),75.3(d,C-7),42.1(s,C-8),35.3(d,C-9),41.7(s,C-10),15.7(t,C-11),32.9(t,C-12),47.3(s,C-13),159.9(s,C-14),118.2(d,C-15),34.3(t,C-16),51.4(d,C-17),20.0(q,C-18),16.2(q,C-19),124.9(s,C-20),139.6(d,C-21),111.1(d,C-22),142.4(d,C-23),28.0(q,C-28),21.5(q,C-29),27.5(q,C-30),170.6(s,3-$COCH_3$),21.3(q,3-$COCH_3$)。以上数据与参考文献对照分析[4],可鉴定该化合物为7-*O*-acetyl-14,15-deoxyhavanensin。

化合物**6** 无色固体(甲醇);EI-MS:m/z 452 $[M]^+$;^{1}H-NMR(400 MHz,$CDCl_3$),δ:7.11(1H,d,J=10.0 Hz,H-1),5.90(1H,d,J=10.0 Hz,H-2),2.75(1H,d,J=12.0 Hz,H-5),5.47(1H,dd,J=12.4,2.4 Hz,H-6),4.08(1H,d,J=2.0 Hz,H-7),2.30(1H,dd,J=11.6,6.0 Hz,H-9),5.58(1H,d,J=2.0 Hz,H-15),2.87(1H,dd,J=10.8,7.2 Hz,H-17),0.83(3H,s,H-18),1.18(3H,s,H-19),7.26(1H,s,H-21),6.29(1H,d-like,H-22),7.39(1H,t-like,H-23),1.29(3H,s,H-28),1.20(3H,s,H-29),1.32(3H,s,H-30),2.19(3H,s,3-OAc);^{13}C-NMR(100 MHz,$CDCl_3$),δ:157.2(d,C-1),126.0(d,C-2),205.0(s,C-3),41.1(s,C-4),46.3(d,C-5),76.8(d,C-6),68.2(d,C-7),44.9(s,C-8),35.6(d,C-9),44.9(s,C-10),16.2(t,C-11),32.2(t,C-12),47.2(s,C-13),160.0(s,C-14),120.6(d,C-15),34.3(t,C-16),51.6(d,C-17),20.6(q,C-18),20.6(q,C-19),124.1(s,C-20),139.7(d,C-21),110.9(d,C-22),142.7(d,C-23),26.6(q,C-28),20.6(q,C-29),31.6(q,C-30),170.5(s,6-$COCH_3$),21.8(q,6-$COCH_3$)。以上数据与参考文献对照分析[5],故鉴定该化合物结构为6α-*O*-acetyl-7-deacetylnimocinol。

化合物**7** 无色固体(甲醇),$C_{28}H_{36}O_5$;EI-MS:m/z 452 $[M]^+$;^{1}H-NMR(400 MHz,$CDCl_3$),δ:7.13(1H,d,J=10.0 Hz,H-1),5.92(1H,d,J=10.0 Hz,H-2),2.22(1H,d,J=11.6 Hz,H-5),4.40(1H,dd,J=11.6,2.4 Hz,H-6),5.38(1H,d,J=2.4 Hz,H-7),2.25(1H,d,J=6.8 Hz,H-9),5.43(1H,d,J=1.6 Hz,H-15),2.85(1H,dd,J=10.4,7.6 Hz,H-17),0.84(3H,s,H-18),1.43(3H,s,H-19),7.27(1H,s,H-21),6.30(1H,d-like,H-22),7.40(1H,t-like,H-23),1.29(3H,s,H-28),1.15(3H,s,H-29),1.33(3H,s,H-30),2.07(3H,s,3-OAc);^{13}C-NMR(100 MHz,$CDCl_3$),δ:157.4(d,C-1),126.2(d,C-2),205.9(s,C-3),40.5(s,C-4),49.9(d,C-5),68.2(d,C-6),79.1(d,C-7),45.4(s,C-8),37.1(d,C-9),43.1(s,C-10),16.4(t,C-11),32.7(t,C-12),47.1(s,C-13),158.5(s,C-14),119.5(d,C-15),34.3(t,C-16),51.6(d,C-17),20.8(q,C-18),20.3(q,C-19),124.4(s,C-20),139.7(d,C-21),111.0(d,C-22),142.6(d,C-23),27.1(q,C-28),20.9(q,C-29),31.9(q,C-30),172.1(s,6-$COCH_3$),21.2(q,6-$COCH_3$)。以上数据与参考文献对照分析[6],可鉴定该化合物为6α-hydroxyazadirone。

化合物**8** 无色固体(甲醇);EI-MS:m/z 452 $[M]^+$;^{1}H-NMR(400 MHz,$CDCl_3$),δ:4.25(1H,d,J=11.2 Hz,H-3),2.11(1H,d,J=8.8 Hz,H-5),5.33(1H,d,J=2.4 Hz,H-7),2.42(1H,d,J=10.8 Hz,H-9),5.40(1H,s,H-15),2.81(1H,d,J=7.6 Hz,H-17),0.81(3H,s,H-18),1.20(3H,s,H-19),7.24(1H,s,H-21),6.28(1H,s,H-22),7.38(1H,s,H-23),1.25(3H,s,H-28),1.29(3H,s,H-29),1.33(3H,s,H-30),2.08(3H,s,3-OAc);^{13}C-NMR(100 MHz,$CDCl_3$),δ:38.4(t,C-1),29.7(t,C-2),79.3(d,C-3),37.7(s,C-4),51.5(d,C-5),23.4(t,C-6),68.3(d,C-7),46.8(s,C-8),41.3(d,C-9),42.8(s,C-10),16.3(t,C-11),32.7(t,C-12),47.1(s,C-13),158.6(s,C-14),119.4(d,C-15),34.4(t,C-16),51.6(d,C-17),19.3(q,C-18),16.6(q,C-19),124.5(s,C-20),139.7(d,C-21),111.0(d,C-22),142.6(d,C-23),26.2(q,C-28),20.6(q,C-29),31.6(q,C-30),172.2(s,6-$COCH_3$),21.3(q,6-$COCH_3$)。以上数据与参考文献对照分析[7],可鉴定该化合物为24-nor-5ξ-13α,17α-chola-14,20,22-triene-3β,7α-diol-21,23-epoxy-4,4,8-trimethyl-3-acetate。

化合物**9** 淡黄色固体(氯仿);EI-MS:m/z 536 $[M]^+$,358,343,327,205,191,175,163,151,137;^{1}

H-NMR(400 MHz, $CDCl_3$), δ: 6.95 ~ 6.87(1H, m, H-2), 6.84 ~ 6.77(1H, m, H-5), 6.95 ~ 6.87(1H, m, H-6), 4.74(1H, d-like, H-7), 3.10(1H, s, H-8), 4.24(1H, t, J = 6.8 Hz, Ha-9), 3.84 ~ 3.82(1H, m, Hb-9), 6.95 ~ 6.87(1H, m, H-2′), 6.84 ~ 6.77(1H, m, H-6′), 4.86(1H, d, J = 4.4 Hz, H-7′), 3.31(1H, d-like, H-8′), 4.12(1H, d, J = 9.2 Hz, Ha-9′), 3.84 ~ 3.82(1H, m, Hb-9′), 6.95 ~ 6.87(1H, m, H-2″), 6.84 ~ 6.77(1H, m, H-5″), 6.95 ~ 6.87(1H, m, H-6″), 4.43(1H, d, J = 6.8 Hz, H-7″), 2.91(1H, d, J = 7.2 Hz, H-8″), 3.84 ~ 3.82(1H, m, Ha-9″), 3.31(1H, d-like, Hb-9″), 3.89(3H, s, 3-OCH_3), 3.89(3H, s, 3′-OCH_3), 3.89(3H, s, 3″-OCH_3); ^{13}C-NMR(100 MHz, $CDCl_3$), δ: 132.7(s, C-1), 108.5(d, C-2), 146.7(s, C-3), 145.1(s, C-4), 119.1(d, C-5), 114.2(d, C-6), 85.8(d, C-7), 54.0(d, C-8), 71.5(t, C-9), 132.7(s, C-1′), 108.3(d, C-2′), 146.4(s, C-3′), 144.5(s, C-4′), 130.2(s, C-5′), 118.3(d, C-6′), 82.0(d, C-7′), 50.0(d, C-8′), 70.9(t, C-9′), 132.9(s, C-1″), 108.6(d, C-2″), 146.7(s, C-3″), 145.2(s, C-4″), 118.9(d, C-5″), 114.2(d, C-6″), 87.7(d, C-7″), 54.3(d, C-8″), 69.6(t, C-9″), 55.9(q, C-3), 55.8(q, C-3′), 55.9(q, C-3″)。以上数据与参考文献对照分析[8], 可鉴定该化合物为 hedyotol-A。

化合物 **10** 淡黄色固体(氯仿), $C_{20}H_{20}O_7$; EI-MS: m/z 372 [M]$^+$, 280, 264, 250, 207, 191, 175, 165, 151, 137; ^{1}H-NMR(400 MHz, $CDCl_3$), δ: 3.45(1H, dt, J = 8.8, 3.6 Hz, H-1), 4.50(1H, dd, J = 9.6, 2.8 Hz, H-2), 4.19(1H, dd, J = 9.6, 4.0 Hz, Ha-4), 4.38 ~ 4.31(1H, m, Hb-4), 3.16 ~ 3.09(1H, m, H-5), 4.62(1H, d, J = 7.2 Hz, H-6), 6.91 ~ 6.79(2H, m, H-2′, 2″), 6.91 ~ 6.79(1H, m, H-5′, 5″), 6.91 ~ 6.79(1H, m, H-6′, 6″), 3.90(6H, s, OCH_3-3′, 3″); ^{13}C-NMR(100 MHz, $CDCl_3$), δ: 45.9(d, C-1), 86.0(d, C-2), 69.9(t, C-4), 48.1(d, C-5), 86.0(d, C-6), 178.3(s, C-8), 130.5(s, C-1′, 1″), 108.4(d, C-2′, 2″), 146.9(s, C-3′, 3″), 145.8(s, C-4′, 4″), 114.4(d, C-5′, 5″), 119.0(d, C-6′, 6″), 55.9(q, C-OCH_3)。以上数据与参考文献对照分析[9], 可鉴定该化合物为 2, 6-bis(3-methoxy-4-hydroxyphenyl)-3, 7-dioxabicyclo[3, 3, 0]octan-8-one。

化合物 **11** 淡黄色固体(氯仿), $C_{20}H_{22}O_6$; EI-MS: m/z 358 [M]$^+$, 341, 327, 205, 189, 175, 163, 151, 137; ^{1}H-NMR(400 MHz, $CDCl_3$), δ: 3.34 ~ 3.29(1H, m, H-1), 4.86(1H, d, J = 5.2 Hz, H-2), 3.82(1H, t, J = 6.8 Hz, Ha-4), 4.12(1H, d, J = 9.2 Hz, Hb-4), 2.91(1H, dd, J = 14.4, 6.8 Hz, H-5), 4.43(1H, d, J = 7.2 Hz, H-6), 3.34 ~ 3.29(1H, m, Ha-8), 3.82(1H, t, J = 6.8 Hz, Hb-8), 7.26 ~ 6.77(1H, m, H-2′), 7.26 ~ 6.77(1H, m, H-5′), 7.26 ~ 6.77(1H, m, H-6′), 7.26 ~ 6.77(1H, m, H-2″), 7.26 ~ 6.77(1H, m, H-5″), 7.26 ~ 6.77(1H, m, H-6″), 3.91(3H, s, 3′-OCH_3), 3.89(3H, s, 3″-OCH_3); ^{13}C-NMR(100 MHz, $CDCl_3$), δ: 50.1(d, C-1), 82.1(d, C-2), 70.9(t, C-4), 54.4(d, C-5), 87.7(d, C-6), 69.7(t, C-8), 130.3(s, C-1′), 108.3(d, C-2′), 146.4(s, C-3′), 144.5(s, C-4′), 114.2(d, C-5′), 118.4(d, C-6′), 132.9(s, C-1″), 108.5(d, C-2″), 146.7(s, C-3″), 145.3(s, C-4″), 114.2(d, C-5″), 119.2(d, C-6″), 55.9(q, 3′-OCH_3), 55.9(q, 3″-OCH_3)。以上数据与参考文献对照分析[8], 可鉴定该化合物为 exo-endo-2, 6-bis(4′-hydroxy-3′-methoxy-phenyl)-3, 7-dioxabicyclo[3, 3, 0]octane。

化合物 **12** 白色固体(氯仿), $C_{30}H_{50}O_3$; EI-MS: m/z 458 [M]$^+$; ^{1}H-NMR(400 MHz, $CDCl_3$), δ: 1.57 ~ 1.51(1H, m, H-5), 1.57 ~ 1.51(1H, m, H-9), 3.61(1H, dt, J = 10.4, 5.2 Hz, H-12), 2.00 ~ 1.94(1H, m, H-13), 2.15 ~ 2.04(1H, m, H-17), 5.15(1H, t, J = 6.8 Hz, H-24), 1.09(3H, s, H-18), 1.03(3H, s, H-19), 1.16(3H, s, H-21), 1.71(3H, s, H-26), 1.64(3H, s, H-27), 0.99(3H, s, H-28), 0.90(3H, s, H-29), 1.05(3H, s, H-30); ^{13}C-NMR(100 MHz, $CDCl_3$), δ: 39.7(t, C-1), 34.0(t, C-2), 218.0(s, C-3), 47.4(s, C-4), 55.2(d, C-5), 19.6(t, C-6), 34.0(t, C-7), 39.6(s, C-8), 49.8(d, C-9), 36.7(s, C-10), 30.9(t, C-11), 70.5(d, C-12), 48.7(d, C-13), 51.6(s, C-14), 31.4(t, C-15), 26.3(t, C-16), 49.3(d, C-17), 17.0(q, C-18), 15.3(q, C-19), 74.9(s, C-20), 26.6(q, C-21), 42.2(t, C-22), 22.0(t, C-23), 124.4(d, C-24), 132.3(s, C-25), 25.8(q, C-26), 17.7(q, C-27), 26.6(q, C-28), 21.0(q, C-29), 15.9(q, C-30)。以上数据与参考文献对照分析[10], 可鉴定该化合物为 betulafolienediolone。

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无花果内生真菌 FL10 中吲哚二酮哌嗪类生物碱的研究

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[摘要] **目的**:研究无花果内生真菌 FL10 的次级代谢产物成分。**方法**:采用反复硅胶柱色谱法、Sephadex LH-20 凝胶色谱法等进行分离纯化,从无花果内生真菌 FL10 的发酵液中分离得到 6 个吲哚二酮哌嗪类生物碱。**结果**:通过理化常数测定和光谱分析,6 个吲哚二酮哌嗪类生物碱鉴定分别为 verruculogen (**1**), cyclotryprostatins B (**2**), fumitremorgin C (**3**), cyclotryprostatin A (**4**), tryprostatin A (**5**), tryprostatin B (**6**)。**结论**:这 6 个吲哚二酮哌嗪类生物碱是首次从无花果内生真菌中分离得到,目前研究表明,无花果内生真菌 *Aspergillus tamarii* 可以作为一种可产生吲哚二酮哌嗪类生物碱的新来源。

[关键词] 内生真菌; 无花果; 吲哚二酮哌嗪; 生物碱
[中图分类号] R284.1 [文献标识码] A [文章编号] 1005-9903(2013)18-0095-04
[doi] 10.11653/syfj2013180095

Indolyl Diketopiperazine Alkaloids Isolated from Endophyic Fungus FL10 of *Ficus carica*

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[收稿日期] 20120103(002)
[基金项目] 高校博士点基金项目(20116125110001);山西省科技攻关项目(20100311092-1)
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