热带亚热带植物学报 2016, 24(1)：99~105
Journal of Tropical and Subtropical Botany

麻楝枝干的化学成分及其α-葡萄糖苷酶抑制活性研究

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摘要：为了解麻楝(*Chukrasia tabularis* A. Juss)中的生物活性成分，采用柱色谱技术从其枝干乙醇提取物中分离得到 10 个化合物，分别鉴定为：3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one (**1**)、6-hydroxy-1,3,5,7-tetramethoxy-9-xanthen-9-one (**2**)、2,6,2′,6′-tetramethoxy-4,4′-bis(2,3-epoxy-1-hydroxypropyl)biphenyl (**3**)、cleomiscosin D (**4**)、chuktabularin A (**5**)、chuktabularin B (**6**)、chubularisin H (**7**)、chubularisin I (**8**)、tabularisin A (**9**)和 tabularisin B (**10**)，其中化合物 **1**~**4** 为首次从麻楝属中分离得到。对体外 α-葡萄糖苷酶的抑制活性进行了测定，结果表明化合物 **1**、**2**、**6**、**7** 和 **9** 对 α-葡萄糖苷酶均具有较好的抑制活性。

关键词：麻楝；枝干；化学成分；α-葡萄糖苷酶抑制活性

doi: 10.11926/j.issn.1005−3395.2016.01.014

Studies on the Chemical Constituents from the Stems of *Chukrasia tabularis* and Their α-Glucosidase Inhibitory Activity

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Abstract: In order to find the bioactive components from the stems of *Chukrasia tabularis*, ten compounds were isolated from its EtOH extract by using chromatographic techniques. On the basis of spectral data, their structures were identified as 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one (**1**), 6-hydroxy-1,3,5,7-tetramethoxy-9*H*-xanthen-9-one (**2**), 2,6,2′,6′-tetramethoxy-4,4′-bis(2,3-epoxy-1-hydroxypropyl) biphenyl (**3**), cleomiscosin D (**4**), chuktabularin A (**5**), chuktabularin B (**6**), chubularisin H (**7**), chubularisin I (**8**), tabularisin A (**9**), and tabularisin B (**10**). Compounds **1**–**4** were isolated from the genus *Chukrasia* for the first time. Furthermore, compounds **1**, **2**, **6**, **7 and 9** exhibited inhibitory activity against α-glucosidase *in vitro*.

Key words: *Chukrasia tabularis*; Stem; Chemical constituent; α-Glucosidase inhibitory activity

麻楝 (*Chukrasia tabularis* A. Juss) 为楝科 (Meliaceae)麻楝属植物，该属为单种属，仅包括麻楝原种及其变种毛麻楝(*C. tabularis* var. *velutina*)[1]，其主要分布于印度、缅甸、斯里兰卡、中南半岛、马来半岛等地，我国云南、广东、海南、广西、西藏等地均有分布。据《中华本草》记载，麻楝的根皮是我国传统中药材，具有疏风清热的功效，主要用于治疗感冒发热。麻楝的主要化学成分为柠檬苦

收稿日期：2015−05−29 **接受日期**：2015−07−13

基金项目：公益性行业(农业)科研专项(201303117)；海南省中药现代化专项(ZY201408)；中国热带农业科学院热带生物技术研究所基本科研业务费(ITBB2015RC03)资助

This work was supported by the Special Project for Agricultural Public Welfare Science Research (Grant No. 201303117), the Special Project for Chinese Traditional Medicine Modernization in Hainan Province (Grant No. ZY201408), and the Basic Research Fund in Institute of Tropical Bioscience and Biotechnology, Chinese Academy of Tropical Agricultural Sciences (Grant No. ITBB2015RC03).

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素、香豆素、黄酮和挥发油等，其中柠檬苦素是麻楝的特征性化学成分[2]。据报道，麻楝中的柠檬苦素类化合物具有抗炎[3–4]、钾离子通道阻断[5–6]、昆虫拒食[7–8]、抗肿瘤[9]等多种药理活性。前期活性筛选中发现麻楝乙醇提取物对α-葡萄糖苷酶具有良好的抑制活性，为了寻找其中具有α-葡萄糖苷酶抑制活性的成分，我们对麻楝枝干乙酸乙酯部分的化学成分进行了研究，从中分离鉴定了10个单体化合物，其中柠檬苦素类化合物6个。本文报道了从麻楝中分离得到的10个化合物，并测定他们对α-葡萄糖苷酶的抑制活性。

1 材料和方法

1.1 材料

麻楝枝干于 2014 年 7 月采集于海南省海口市，经中国热带农业科学院热带生物技术研究所刘寿柏博士鉴定为麻楝(*Chukrasia tabularis* A. Juss)，凭证标本(CTHK201407)存放于中国热带农业科学院热带生物技术研究所。

1.2 仪器和试剂

化合物分离采用青岛海洋化工厂的薄层色谱硅胶板(GF_{254})和柱色谱硅胶(200~300和60~80目); Merck公司的Sephadex LH-20和RP-18填料。旋光度测定采用Autopol III旋光仪；质谱测定采用Autospec-3000质谱仪；核磁共振采用瑞士Bruker公司的Brucker AV-500型超导核磁仪(TMS内标); 美国宝特公司ELX-800酶标仪，超净工作台为上海博讯实业有限公司医疗设备厂产品；α-葡萄糖苷酶(α-Glucosidase, EC 3.2.1.2)、4-硝基苯酚-α-D-吡喃葡萄糖苷(4-Nitrophenyl-α-D-glucopyranoside, PNPG)、阿卡波糖(Acarbose)均购自Sigma公司。

1.3 提取和分离

麻楝枝干(110 kg)晒干后粉碎，用95%乙醇冷浸提取3次，室温，每次7 d；过滤，合并滤液后经真空减压浓缩得粗浸膏，将其分散于水中成悬浊液，依次用石油醚、乙酸乙酯、正丁醇萃取，分别得石油醚萃取物30 g、乙酸乙酯萃取物1700 g、正丁醇萃取物800 g。乙酸乙酯萃取物(1700 g)采用硅胶柱色谱，以石油醚-乙酸乙酯(1∶0~0∶1)梯度洗脱，分段收集得到18个流分(Fr.1~ Fr.18)。Fr.17 (120 g)继续采用硅胶(硅胶H)减压柱色谱，以氯仿-甲醇(1∶0~0∶1)梯度洗脱，分段收集得到18个流分(Fr.17-1~Fr.17-18)。Fr.17-1 (7.0 g)经加压ODS (甲醇-水3∶7~1∶0)梯度洗脱，得21个流分(Fr.17-1-1~Fr.17-1-21)。经反复Sephadex LH-20 (氯仿-甲醇1∶1)柱色谱以及加压硅胶柱色谱得到化合物**1** (1.5 mg)、**2** (1.8 mg)、**3** (20.0 mg)、**4** (7.0mg)、**5** (5.2 mg)和**6** (9.0 mg); Fr.15 (268 g)采用硅胶(硅胶H)减压柱色谱，以氯仿-乙酸乙酯(1∶0~0∶1)梯度洗脱，分段收集得到8个流分(Fr.15-1~Fr.15-8)。Fr. 15-2 (36.8 g)经MCI (甲醇-水7∶1~1∶0)梯度洗脱，得到6个流分(Fr.15-2-1~Fr.15-2-6)。Fr. 15-2-3 (3.5g)经加压ODS (甲醇-水3∶1~1∶0)梯度洗脱，获得20个流分(Fr. 15-2-3-1~Fr. 15-2-3-20)。经反复Sephadex LH-20 (氯仿-甲醇1∶1)色谱及硅胶柱色谱得到化合物**7** (5.4 mg)、**8** (4.3 mg)、**9** (550.0 mg)和**10** (3.0 mg)。

1.4 α-葡萄糖苷酶抑制活性测定方法

本测试在紫外分光光度计上进行，反应体系参照Jong-Anurakkun等[10]的方法，优化后的测试方法为：0.5 mL的磷酸钾缓冲液(0.1 mmol L^{-1}，pH=6.8)，加入100 μL的α-葡萄糖苷酶(0.2 U mL^{-1})和0.5 mL样品溶液混匀。在37°C恒温15 min后，再加入0.5 mL的PNPG (2.5 mmol L^{-1})，混匀后37℃恒温15 min。最后加入1 mL的Na_2CO_3溶液(0.2 mol L^{-1})终止反应。以阿卡波糖作为阳性对照，于405 nm波长下测反应液的OD值，重复3次取平均值。计算样品对α-葡萄糖苷酶的抑制率：抑制率(%)=[$A_{空白}$−($A_{样品}$−$A_{背景}$)]/$A_{空白}$×100%。$A_{空白}$为不加待测样品反应后的吸光值，$A_{样品}$为加入待测样品反应后的吸光值，$A_{背景}$为只加待测样品反应后的吸光值。

1.5 结构鉴定

3-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl) propan-1-one (**1**)　白色粉末; ESI-MS *m/z*: 249.1 $[M + Na]^+$, 225.3 $[M - H]^-$; 推断分子式为$C_{11}H_{14}O_5$; ^{1}H MNR ($CDCl_3$, 500 MHz): δ 7.26 (2H, d, *J* = 2.4 Hz, H-2, H-6), 4.04 (2H, t, *J* = 5.4 Hz, H-9), 3.96 (6H, s, 3, 5, 2×OCH_3), 3.20 (2H, t, *J* = 5.4 Hz, H-8); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 128.7 (C-1), 105.8 (C-2, 6), 147.2 (C-3, C-5), 140.5 (C-4), 199.3 (C-7), 40.3 (C-8), 58.7 (C-9), 56.9 (3, 5, 2×OCH_3)。以上波谱数据与文献[11]报道基本一致，故鉴定为3-hydroxy-1-(4-hydroxyl-3,5-dimethoxyphenyl)propan-1-one。

6-Hydroxy-1,3,5,7-tetramethoxy-9*H*-xanthen-

9-one (**2**)　红色粉末; ESI-MS *m/z*: 333.2 $[M + H]^+$; 推断分子式为$C_{17}H_{16}O_7$; ^{1}H MNR ($CDCl_3$, 500 MHz): δ 7.50 (1H, s, H-8), 6.60 (1H, d, *J* = 2.3 Hz, H-4), 6.38 (1H, d, *J* = 2.3 Hz, H-2), 4.12 (3H, s, 5-OCH_3), 4.11 (3H, s, 1-OCH_3), 3.99 (3H, s, 3-OCH_3), 3.94 (3H, s, 7-OCH_3); ^{13}C MNR ($CDCl_3$, 125 MHz): δ 161.7 (C-1), 95.3 (C-2), 164.4 (C-3), 92.7 (C-4), 159.5 (C-4a), 134.0 (C-5), 143.8 (C-6), 144.5 (C-7), 100.7 (C-8), 115.6 (C-8a), 174.5 (C-9), 106.7 (C-9a), 144.5 (C-10a), 56.4 (1-OCH_3), 56.3 (3-OCH_3), 61.6 (5-OCH_3), 55.7 (7-OCH_3)。以上波谱数据与文献[12]报道基本一致，故鉴定为6-hydroxy-1,3,5,7-tetramethoxy-9*H*-xanthen-9-one。

2,6,2′,6′-Tetramethoxy-4,4′-bis(2,3-epoxy-1-hydroxypropyl)biphenyl (**3**)　无色油状物; ESI-MS *m/z*: 441.3 $[M + Na]^+$; 推断分子式为$C_{22}H_{26}O_8$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.61 (4H, s, H-3, 3′, 5, 5′), 5.52 (2H, s, 7, 7′, 2×OH), 4.75 (2H, d, *J* = 4.2 Hz, H-7, 7′), 4.30 (2H, m, H-9H_b, $H_{b'}$), 3.93 (12H, s, 2, 2′, 6, 6′, 4×OCH_3), 3.90 (2H, m, H-9H_a, $H_{a'}$), 3.12 (2H, m, H-8, 8′); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.9 (C-1, 1′), 147.0 (C-2, 2′, 6, 6′), 102.5 (C-3, 3′, 5, 5′), 134.1 (C-4, 4′), 86.0 (C-7, 7′), 54.2 (C-8, 8′), 71.7 (C-9, 9′), 56.3 (2, 2′, 6, 6′, 4×OCH_3)。以上波谱数据与文献[13]报道基本一致，故鉴定为2,6,2′,6′-tetramethoxy-4,4′-bis-(2,3-epoxy-1-hydroxypropyl)biphenyl。

Cleomiscosin D (**4**)　白色粉末; ESI-MS *m/z*: 439.2 $[M + Na]^+$; 推断分子式为$C_{21}H_{20}O_9$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (1H, d, *J* = 9.5 Hz, H-4), 6.90 (1H, s, H-5), 6.73 (2H, s, H-2′, 6′), 6.33 (1H, d, *J* = 9.5 Hz, H-3), 4.95 (1H, d, *J* = 8.0 Hz, H-7′), 4.36 (1H, m, H-8′), 3.77 (6H, s, 3′, 5′, 2×OCH_3), 3.75 (3H, s, 4-OCH_3), 3.63 (1H, m, H-9a), 3.39 (1H, m, H-9b); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.1 (C-2), 113.3 (C-3), 144.7 (C-4), 100.8 (C-5), 145.3 (C-6), 137.1 (C-7), 131.5 (C-8), 138.2 (C-9), 111.3 (C-10), 125.8 (C-1′), 105.7 (C-2′, 6′), 148.0 (C-3′, 5′), 136.3 (C-4′), 76.6 (C-7′), 77.8 (C-8′), 59.9 (C-9′), 55.9 (4-OCH_3), 56.2 (3′, 5′, 2×OCH_3)。以上波谱数据与文献[14]报道基本一致，故鉴定为cleomiscosin D。

Chuktabularin A (**5**)　白色无定形粉末; $[\alpha]_D^{28}$ +238 ° (*c* 0.1, $CHCl_3$), ESI-MS *m/z*: 799.4 $[M + Na]^+$; 推断分子式为$C_{38}H_{48}O_{17}$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (1H, br s, H-21), 7.37 (1H, br t, *J* = 1.4 Hz, H-23), 6.50 (1H, br d, *J* = 1.4 Hz, H-22), 6.16 (1H, s, H-17), 5.67 (1H, d, *J* = 3.3 Hz, H-11), 5.63 (1H, d, *J* = 3.3 Hz, H-12), 5.23 (1H, s, H-3), 4.64 (1H, s, 1-OH), 4.63 (1H, s, H-30), 3.62 (3H, s, 7-OCH_3), 3.27 (1H, s, 9-OH), 3.10 (1H, dd, *J* = 11.7, 7.6 Hz, H-14), 2.58 (1H, br d, *J* = 12.1 Hz, H-5), 2.53 (1H, dd, *J* = 11.7, 7.6 Hz, H-15β), 2.47 (3H, s, 3-OAc), 2.44 (1H, br d, *J* = 16.5 Hz, H-6a), 2.22 (1H, dd, *J* = 16.5, 12.1 Hz, H-6b), 2.10 (3H, s, 17-OAc), 2.08 (3H, s, 12-OAc), 2.07 (3H, s, 2-OAc), 1.94 (3H, s, 11-OAc), 1.90 (1H, d, *J* = 11.7 Hz, H-15α), 1.84 (1H, d, *J* = 11.3 Hz, H-29a), 1.80 (1H, d, *J* = 11.3 Hz, H-29b), 1.63 (3H, s, H-32), 1.19 (3H, s, H-19), 0.91 (3H, s, H-18), 0.77 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 84.6 (C-1), 82.3 (C-2), 83.5 (C-3), 45.5 (C-4), 41.3 (C-5), 34.3 (C-6), 173.3 (C-7), 90.2 (C-8), 76.3 (C-9), 52.7 (C-10), 72.5 (C-11), 73.4 (C-12), 41.8 (C-13), 44.9 (C-14), 35.6 (C-15), 71.3 (C-17), 19.1 (C-18), 18.9 (C-19), 122.5 (C-20), 140.7 (C-21), 109.7 (C-22), 143.2 (C-23), 16.2 (C-28), 40.1 (C-29), 71.2 (C-30), 110.4 (C-31), 17.8 (C-32), 51.9 (7-OCH_3), 2-OAc [(169.8), (21.1)], 3-OAc [(169.6), (21.2)], 11-OAc [(169.6), (21.1)], 12-OAc [(169.3), (20.7)], 17-OAc [(168.9), (20.6)]。以上波谱数据与文献[15]报道基本一致，故鉴定为chuktabularin A。

Chuktabularin B (**6**)　白色无定形粉末; $[\alpha]_D^{28}$ +135 ° (*c* 0.1, $CHCl_3$), ESI-MS *m/z*: 783.3 $[M + Na]^+$; 推断分子式为$C_{37}H_{44}O_{17}$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (1H, br s, H-21), 7.45 (1H, br t, *J* = 1.3 Hz, H-23), 6.45 (1H, br d, *J* = 1.3 Hz, H-22), 6.09 (1H, s, H-17), 5.66 (1H, d, *J* = 3.6 Hz, H-11), 5.45 (1H, d, *J* = 3.6 Hz, H-12), 5.31 (1H, s, H-3), 4.96 (1H, d, *J* = 12.5 Hz, H-19a), 4.79 (1H, s, 1-OH), 4.61 (1H, s, H-30), 4.16 (1H, d, *J* = 12.5 Hz, H-19b), 3.37 (1H, s, 9-OH), 3.29 (1H, dd, *J* = 11.7, 8.0 Hz, H-14), 2.56 (1H, dd, *J* = 11.7, 8.0 Hz, H-15β), 2.45 (3H, s, 3-OAc), 2.29 (1H, m, H-6), 2.11 (1H, d, *J* = 11.7 Hz, H-29a), 2.10 (3H, s, 11-OAc), 2.09 (3H, s, 2-OAc), 2.09 (3H, s, 12-OAc), 2.09 (3H, s, 17-OAc), 2.05 (1H, m, H-5), 2.01 (1H, dd, *J* = 11.7, 11.7 Hz, H-15α), 1.99 (1H, d, *J* = 11.7 Hz, H-29b), 1.65 (3H, s, H-32), 0.91 (3H, s, H-18), 0.90 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 85.2 (C-1), 80.9 (C-2), 82.6 (C-3), 45.2 (C-4), 40.5 (C-5), 30.9 (C-6), 173.1 (C-7), 89.6 (C-8),

75.2 (C-9), 52.1 (C-10), 71.4 (C-11), 72.0 (C-12), 41.1 (C-13), 44.2 (C-14), 35.7 (C-15), 71.3 (C-17), 19.4 (C-18), 68.7 (C-19), 122.0 (C-20), 140.0 (C-21), 109.0 (C-22), 142.9 (C-23), 15.0 (C-28), 38.4 (C-29), 71.1 (C-30), 110.9 (C-31), 18.7 (C-32), 2-OAc [(169.8), (20.8)], 3-OAc [(169.4), (21.1)], 11-OAc [(170.9), (20.4)], 12-OAc [(170.0), (20.6)], 17-OAc [(169.1), (20.3)]。以上波谱数据与文献[15]报道基本一致，故鉴定为chuktabularin B。

Chubularisin H (**7**) 白色无定形粉末; $[\alpha]_D^{28}$+116 °(*c* 0.1, $CHCl_3$), ESI-MS *m/z*: 911.5 $[M + Na]^+$; 推断分子式为$C_{43}H_{52}O_{20}$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (1H, br t, *J* = 1.7 Hz, H-21), 7.39 (1H, br t, *J* = 1.7 Hz, H-23), 7.06 (1H, br d, *J* = 3.0 Hz, H-15), 6.51 (1H, br d, *J* = 1.7 Hz, H-22), 6.43 (1H, s, H-17), 5.92 (1H, s, H-6), 5.46 (1H, s, H-3), 5.36 (1H, s, H-30), 5.32 (1H, br d, *J* = 3.5 Hz, H-12), 4.22 (1H, d, *J* = 3.5 Hz, H-11), 3.79 (3H, s, 7-OCH_3), 3.49 (1H, s, 2-OH), 2.91 (1H, m, H-2′), 2.88 (1H, s, H-5), 2.85 (1H, s, 1-OH), 2.65 (1H, dd, *J* = 6.8, 3.0 Hz, H-18a), 2.51 (1H, m, H-2″), 2.22 (3H, s, 6-OAc), 2.20 (3H, s, 3-OAc), 2.15 (1H, d, *J* = 10.9 Hz, H-29a), 1.95 (1H, d, *J* = 10.9 Hz, H-29b), 1.67 (3H, s, 12-OAc), 1.66 (3H, s, H-32), 1.43 (1H, d, *J* = 6.8 Hz, H-18b), 1.34 (3H, s, H-19), 1.31 (3H, d, *J* = 7.3 Hz, H-4′), 1.25 (3H, d, *J* = 6.6 Hz, H-3′), 1.19 (3H, d, *J* = 6.9 Hz, H-4″), 1.17 (3H, d, *J* = 6.9 Hz, H-3″), 1.00 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 83.1 (C-1), 76.7 (C-2), 86.0 (C-3), 44.9 (C-4), 43.1 (C-5), 70.8 (C-6), 171.7 (C-7), 78.3 (C-8), 90.8 (C-9), 45.1 (C-10), 74.9 (C-11), 66.4 (C-12), 31.1 (C-13), 30.9 (C-14), 69.3 (C-15), 167.0 (C-16), 71.4 (C-17), 18.6 (C-18), 15.2 (C-19), 122.3 (C-20), 142.1 (C-21), 109.8 (C-22), 143.5 (C-23), 15.4 (C-28), 40.1 (C-29), 70.0 (C-30), 119.6 (C-31), 16.3 (C-32), 53.7 (7-OCH_3), 15-isobutyryloxyl [177.9 (C-1′), 34.2 (C-2′), 19.8 (C-3′), 17.9 (C-4′)], 30-isobutyryloxyl [173.4 (C-1″), 33.9 (C-2″), 19.5 (C-3″), 18.9 (C-4″)], 3-OAc [(169.2), (21.1)], 6-OAc [(169.2), (21.2)], 12-OAc [(170.7), (19.7)]。以上波谱数据与文献[16]报道基本一致，故鉴定为chubularisin H。

Chubularisin I (**8**) 白色无定形粉末; $[\alpha]_D^{28}$ +124 °(*c* 0.1, $CHCl_3$), ESI-MS *m/z*: 839.3 $[M + Na]^+$; 推断分子式为$C_{40}H_{48}O_{18}$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (1H, br s, H-21), 7.39 (1H, br s, H-23), 7.21 (1H, br d, *J* = 2.8 Hz, H-15), 6.49 (1H, br s, H-22), 6.43 (1H, s, H-17), 5.52 (1H, s, H-3), 5.40 (1H, s, H-30), 5.13 (1H, br d, *J* = 3.2 Hz, H-12), 4.17 (1H, d, *J* = 3.2 Hz, H-11), 3.80 (1H, s, 2-OH), 3.76 (3H, s, 7-OCH_3), 2.92 (1H, m, H-2′), 2.84 (1H, s, 1-OH), 2.65 (1H, d, *J* = 16.7 Hz, H-6a), 2.64 (1H, dd, *J* = 6.8, 2.8 Hz, H-18a), 2.58 (1H, d, *J* = 12.4 Hz, H-5), 2.45 (1H, d, *J* = 16.7 Hz, H-6b), 2.32 (2H, q, *J* = 7.7 Hz, H-2″), 2.20 (3H, s, 3-OAc), 1.91 (2H, s, H-29), 1.66 (3H, s, H-32), 1.66 (3H, s, 12-OAc), 1.43 (1H, d, *J* = 6.8 Hz, H-18b), 1.37 (3H, d, *J* = 7.0 Hz, H-4′), 1.30 (3H, s, H-19), 1.24 (3H, d, *J* = 7.0 Hz, H-3′), 1.19 (3H, t, *J* = 7.1 Hz, H-3″), 0.82 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 83.1 (C-1), 76.5 (C-2), 85.8 (C-3), 45.0 (C-4), 38.2 (C-5), 33.1 (C-6), 173.9 (C-7), 78.5 (C-8), 90.6 (C-9), 44.1 (C-10), 75.0 (C-11), 66.6 (C-12), 31.2 (C-13), 30.8 (C-14), 69.9 (C-15), 167.1 (C-16), 71.5 (C-17), 18.8 (C-18), 14.7 (C-19), 122.1 (C-20), 142.2 (C-21), 109.8 (C-22), 143.5 (C-23), 14.3 (C-28), 38.9 (C-29), 70.7 (C-30), 119.9 (C-31), 16.4 (C-32), 52.6 (7-OCH_3), 15-isobutyryl-oxyl [178.0 (C-1′), 34.2 (C-2′), 19.5 (C-3′), 17.8 (C-4′)], 30-propionyloxyl [171.1 (C-1″), 27.4 (C-2″), 9.2 (C-3″)], 3-OAc [(169.3), (21.1)], 12-OAc [(170.8), (20.0)]。以上波谱数据与文献[16]报道基本一致，故鉴定为chubularisin I。

Tabularisin A (**9**) 白色无定形粉末; $[\alpha]_D^{28}$ +185 °(*c* 0.1, $CHCl_3$), ESI-MS *m/z*: 883.4 $[M + Na]^+$; 推断分子式为$C_{41}H_{48}O_{20}$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (1H, br s, H-21), 7.39 (1H, br s, H-23), 7.09 (1H, d, *J* = 3.0 Hz, H-15), 6.50 (1H, d, *J* = 2.0 Hz, H-22), 6.43 (1H, s, H-17), 5.90 (1H, s, H-6), 5.46 (1H, s, H-3), 5.36 (1H, s, H-30), 5.31 (1H, br d, *J* = 3.6 Hz, H-12), 4.22 (1H, d, *J* = 3.6 Hz, H-11), 3.79 (3H, s, 7-OCH_3), 3.36 (1H, s, 2-OH), 2.87 (1H, s, H-5), 2.83 (1H, s, 1-OH), 2.66 (1H, dd, *J* = 6.8, 3.0 Hz, H-18a), 2.50~2.55 (1H, m, H-2′), 2.33 (3H, s, 15-OAc), 2.21 (3H, s, 6-OAc), 2.18 (3H, s, 3-OAc), 2.15 (1H, d, *J* = 10.9 Hz, H-29b), 1.94 (1H, d, *J* = 10.9 Hz, H-29a), 1.66 (3H, s, H-32), 1.66 (3H, s, 12-OAc), 1.42 (1H, d, *J* = 6.8 Hz, H-18b), 1.33 (3H, s, H-19), 1.19 (3H, d, *J* = 7.2 Hz, H-4′), 1.18 (3H, d, *J* = 7.2 Hz, H-3′), 0.98 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 83.0 (C-1), 76.6 (C-2), 85.9 (C-3), 44.8 (C-4), 43.1 (C-5), 70.7 (C-6), 171.6 (C-7), 78.2 (C-8), 90.7 (C-9), 45.1 (C-10),

74.9 (C-11), 66.3 (C-12), 31.0 (C-13), 30.7 (C-14), 69.7 (C-15), 166.9 (C-16), 71.4 (C-17), 18.6 (C-18), 15.2 (C-19), 122.1 (C-20), 142.1 (C-21), 109.7 (C-22), 143.5 (C-23), 15.3 (C-28), 40.0 (C-29), 70.1 (C-30), 119.6 (C-31), 16.3 (C-32), 53.7 (7-OCH_3), 30-isobutyryloxyl [173.5 (C-1′), 34.0 (C-2′), 19.5 (C-3′), 18.9 (C-4′)], 3-OAc [(169.1), (21.1)], 6-OAc [(169.2), (21.1)], 12-OAc [(170.7), (19.7)], 15-OAc [(172.3), (21.6)]。以上波谱数据与文献[17]报道基本一致，故鉴定为tabularisin A。

Tabularisin B (**10**)　白色无定形粉末; $[\alpha]_D^{28}$ +264 °(*c* 0.1, $CHCl_3$), ESI-MS *m/z*: 841.4 $[M + Na]^+$; 推断分子式为$C_{39}H_{46}O_{19}$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (1H, br s, H-21), 7.53 (1H, br s, H-23), 7.08 (1H, d, *J* = 2.8 Hz, H-15), 6.56 (1H, br s, H-22), 6.42 (1H, s, H-17), 5.47 (1H, s, H-3), 5.36 (1H, s, H-30), 5.34 (1H, s, H-6), 4.25 (1H, d, *J* = 3.5 Hz, H-11), 4.03 (1H, d, *J* = 3.5 Hz, H-12), 3.81 (3H, s, 7-OCH_3), 3.38 (1H, s, 2-OH), 2.93 (1H, s, 1-OH), 2.77 (1H, s, H-5), 2.50~2.55 (1H, m, H-2′), 2.46 (1H, dd, *J* = 6.7, 2.8 Hz, H-18a), 2.33 (3H, s, 15-OAc), 2.23 (3H, s, 6-OAc), 2.18 (3H, s, 3-OAc), 2.14 (1H, d, *J* = 10.8 Hz, H-29b), 1.96 (1H, d, *J* = 10.8 Hz, H-29a), 1.67 (3H, s, H-32), 1.37 (1H, m, H-18b), 1.34 (3H, s, H-19), 1.21 (3H, d, *J* = 7.0 Hz, H-4′), 1.19 (3H, d, *J* = 7.0 Hz, H-3′), 0.97 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 83.2 (C-1), 76.4 (C-2), 85.8 (C-3), 44.8 (C-4), 42.9 (C-5), 71.1 (C-6), 171.4 (C-7), 77.9 (C-8), 91.1 (C-9), 45.3 (C-10), 76.5 (C-11), 65.1 (C-12), 34.7 (C-13), 31.7 (C-14), 69.8 (C-15), 167.1 (C-16), 71.4 (C-17), 18.3 (C-18), 15.2 (C-19), 122.1 (C-20), 142.7 (C-21), 108.9 (C-22), 145.0 (C-23), 15.4 (C-28), 39.9 (C-29), 70.0 (C-30), 119.4 (C-31), 16.3 (C-32), 53.9 (7-OCH_3), 30-isobutyryloxyl [173.6 (C-1′), 34.0 (C-2′), 19.6 (C-3′), 18.9 (C-4′)], 3-OAc [(169.1), (21.2)], 6-OAc [(169.6), (21.2)], 15-OAc [(172.4), (21.6)]。以上波谱数据与文献[17]报道基本一致，故鉴定为tabularisin B。

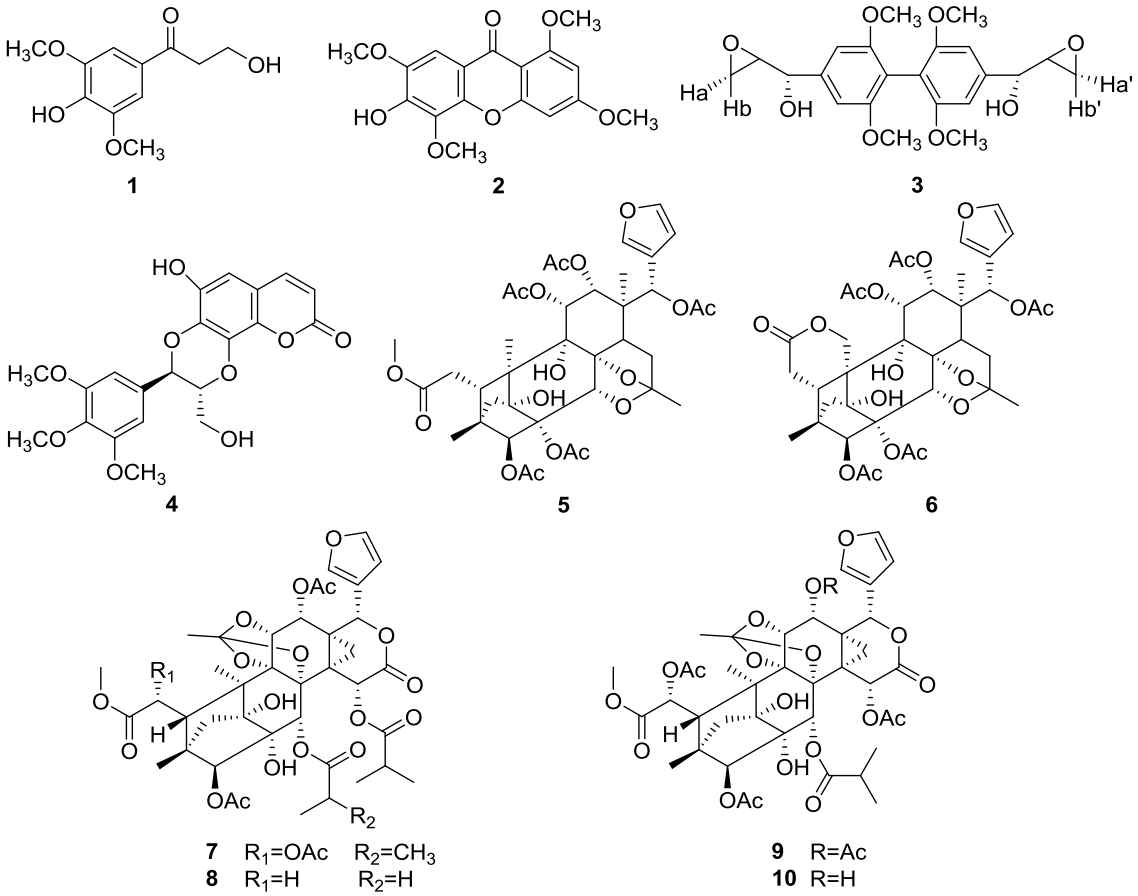

图1 化合物**1**~**10**的结构

Fig. 1 Structures of compounds **1**–**10**

1.6 化合物对α-葡萄糖苷酶抑制活性测试

本试验采用体外抑制法测定了化合物**1**~**10**的α-葡萄糖苷酶抑制活性，结果表明，麻楝中柠檬苦素类化合物表现出明显的对α-葡萄糖苷酶的抑制活性，且部分柠檬苦素类化合物的活性优于阳性对照阿卡波糖；另外，部分木脂素类化合物也表现出一定的α-葡萄糖苷酶的抑制活性(表1)。

表1 化合物的α-葡萄糖苷酶抑制活性(IC_{50})

Table 1 α-Glucosidase inhibitory activity of compounds (IC_{50})

化合物 Compound	IC_{50} (μg mL^{-1})	化合物 Compound	IC_{50} (μg mL^{-1})
1	353.2	**7**	505.1
2	362.2	**8**	—
3	—	**9**	377.5
4	—	**10**	—
5	—	阿卡波糖 Acarbose	794.5
6	338.0		

2 结果和讨论

本文采用多种色谱技术，从麻楝枝干提取物中分离得到了10个化合物，分别鉴定为：3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one (**1**)、6-hydroxy-1,3,5,7-tetramethoxy-9*H*-xanthen-9-one (**2**)、2,6,2′,6′-tetramethoxy-4,4′-bis(2,3-epoxy-1-hydroxypropyl)biphenyl (**3**)、cleomiscosin D (**4**)、chuktabularin A (**5**)、chuktabularin B (**6**)、chubular-isin H (**7**)、chubularisin I (**8**)、tabularisin A (**9**)和tabularisin B (**10**)，其中有6个为柠檬苦素类化合物，化合物**1~4**为首次从麻楝属植物中分离得到。对所得化合物进行了体外α-葡萄糖苷酶抑制活性测试，结果表明，化合物**1**、**2**、**6**、**7**和**9**均具有较好的抑制活性，本文为首次报道柠檬苦素类化合物具有体外抑制α-葡萄糖苷酶的活性。同时，据文献报道，化合物**1**具有抗氧化活性[18]和细胞毒活性[19]，化合物**4**具有抗炎活性[20]，化合物**7**具有较强的钾离子通道抑制活性[16]，但并未见其他化合物生物活性的报道。本研究结果为进一步挖掘麻楝的药用价值提供了科学依据。

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