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中华青牛胆的化学成分研究

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摘　要: 对中华青牛胆(*Tinospora sinensis*)的化学成分进行研究。从其 95% 乙醇提取物的乙酸乙酯部位分离得到了 6个化合物, 根据化合物的理化性质和光谱数据鉴定其结构分别为: 反式丁香苷(**1**)、3′-去甲基-连翘苷(**2**)、半蒂苷(**3**)、香草醛(**4**)、胡萝卜苷(**5**)、β-谷甾醇(**6**)。以上化合物均为首次从该植物中分离得到。

关键词: 中华青牛胆; 化学成分; 丁香苷; 连翘苷

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Chemical constituents from *Tinospora sinensis*

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Abstract To study the chemical constituents from *Tinospora sinensis*, this paper aimed at searching for bioactive natural products. Six compounds were isolated from *Tinospora sinensis* and their structures were identified by means of spectroscopic analysis as: rans-syringin (**1**), 3′-Demethy-phillyrin (**2**), sesquiterpene glycoside (**3**), vanillin (**4**), daucosterol (**5**), β-sitosterol (**6**).

Key words *Tinospora sinensis*; chemical constituents; syringin; phillyrin

中华青牛胆[*Tinospora sinensis*. (Lour.)Merr]为防己科青牛胆属植物[1]。青牛胆属是一个相对较大的缠绕藤本属, 全属约 20余种, 主要分布在东半球热带及亚热带地区, 我国有 6个种 2个变种, 集中分布在西南和南部各省区[2]。该属植物的块根、藤茎常作为中药入药。中华青牛胆的藤茎味苦、性凉, 具有调补气血、舒筋活络、镇心安神的功效[1,2]。据文献调研, 该植物除了 Rachel W. Li, G. David Lin等对其抗炎活性[3]和 P. N. Manjrekar, C. I. Jolly, S. Narayanan对其免疫调节活性[4]的研究报道外, 未见其化学成分的系统研究。因此, 我们对其藤茎的化学成分进行了研究, 从中共分离得到了 6个化合物, 通过理化常数的测定, 各种光谱数据的分析, 确定它们的结构分别为: 反式丁香苷(**1**)、3′-去甲基-连翘苷(**2**)、半蒂苷(**3**)、香草醛(**4**)、胡萝卜苷(**5**)、β-谷甾醇(**6**)。

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1　仪器与材料

EI-MS用 VG Auto Spec-3000型质谱仪测定。NMR用 Bruker AM-400和 Bruker DRX-500超导核磁共振仪测定, TMS为内标。凝胶为 Sephadex LH-20, 反相 RP-18。薄层色谱, 柱色谱硅胶、硅胶 GF_{254} 均为青岛海洋化工厂生产。

2　提取和分离

采自云南西双版纳的中华青牛胆干燥藤茎 13 kg, 经 95% 乙醇回流提取三次, 合并提取液浓缩至小体积后再用乙酸乙酯萃取得 120 g膏状物, 经硅胶柱色谱氯仿和甲醇梯度洗脱, RP-18, Sephadex LH-20柱色谱等, 从中共分离得到 6个化合物。

3　结构鉴定

化合物 **1**(**cis-Syringin**)　$C_{17}H_{24}O_9$, 白色针晶(甲醇), EI-MS *m/z*: 372 $[M]^+$; ^{1}H NMR (500MHz, CD_3OD) δ: 3.21(1H, m, H-5glc), 3.39(1H, m, H-2glc), 3.41(1H, m, H-4glc), 3.67(2H, m, H-6glc),

3.85(6H, s, 2-OCH_3), 4.22(2H, d, J = 5.7 Hz, H-9), 4.81(1H, d, J = 9.0 Hz, H-1glc), 5.80(1H, dt, J = 15.8, 5.7 Hz, H-8), 6.52(1H, J = 15.8 Hz, H-7), 6.55(2H, s, H-2和 H-6)。^{13}C NMR (125.0 MHz, CD_3OD) δ 136.1(s, C-1), 135.3(s, C-4), 105.5(d, C-3和 C-5), 154.3(s, C-2和 C-6), 130.1(d, G-7), 131.3(d, C-8), 62.6(t, C-9), 57.1(q, 2-OCH3), 105.4(C-1glc), 75.7 (C-2glc), 78.4(C-3glc), 71.4 (C-4glc), 77.8(C-5glc), 63.6(C-6glc)。以上数据与文献[5]报道一致, 故确定化合物 **1**为反式丁香甙。

化合物 **2**(**3′-Demethy-phillyrin**)　$C_{26}H_{32}O_{11}$, 白色晶体 (氯仿-甲醇), EI-MS m/z: 520 $[M]^+$; ^{1}H NMR (400 MHz, Me_2CO-d_6) δ 3.09(1H, m, H-8), 3.09(1H, m, H-8′), 3.74(3H, s, CH_3O-4′), 3.76 (3H, s, CH_3O-4), 3.81(2H, m, H-9′), 3.83(2H, m, H-9), 4.66(1H, d, J = 3.4 Hz, H-7), 4.66(1H, d, J = 3.4 Hz, H-7′), 6.78(1H, d, J = 8.0 Hz, H-5′), 6.83(1H, d, J = 8.0 Hz, H-6′), 6.89(1H, d, J = 8.3 Hz, H-6), 6.98(1H, s, H-2′), 7.03(1H, s, H-2), 7.11(1H, d, J = 8.3 Hz, H-5), 4.70(1H, m, H-1glc), 3.08-3.44(4H, m, H-5glc), 3.55(1H, m, H-6αglc)。 3.76(1H, m, H-6βglc)。^{13}C NMR (100 MHz, MeCO-d_6) δ 137.5(s, C-1), 133.8(s, C-1′), 111.6(d, C-2), 110.7(d, C-2′), 147.5(s, C-3), 147.4(s, C-3′), 151.0(s, C-4), 149.1(s, C-4′), 117.9(d, C-5), 115.6(d, C-5′), 119.6(d, C-6), 119.2(d, C-6′), 89.6(d, C-7), 86.4(d, C-7′), 55.5 (d, C-8), 55.3(d, C-8′), 72.4(t, C-9), 72.3(t, C-9′), 102.8(d, C-1glc), 74.8(d, C-2glc), 77.8(d, C-3glc), 71.4(d, C-4glc), 77.9(d, C-5glc), 62.7(t, C-6glc)。以上数据与文献[6]报道一致, 故确定化合物 **2**为 3′-去甲基-连翘甙。

化合物 **3**(**Sesquiterpene glycoside**)　$C_{21}H_{32}O_7$, 白色针状结晶, ESI-MS m/z: 419 $[M+Na]^+$; ^{1}H NMR (400 MHz, Me_2CO-d_6) δ 0.92(3H, s, H-13), 1.08(3H, s, H-12), 1.11(3H, s, H-15), 1.19(2H, m, H-8), 1.74(1H, m, H-7), 1.98(1H, d, J = 1.3, H-5), 1.92(3H, m, H-14), 2.04 (2H, m, H-9), 2.65 (1H, dd, J = 6.7, 1.3 Hz, H-1), 3.01(1H, brs, H-6), 5.64(1H, d, J = 1.3 Hz, H-3), 3.74(1H, d, J = 9.6 Hz, H-1glc), 4.47(1H, m, H-2glc), 3.03(1H, m, H-3glc), 3.54(1H, m, H-4glc), 3.10(1H, m, H-5glc), 3.24(2H, m, H-6glc)。^{13}C NMR (100 MHz, Me_2CO-d_6) δ 57.6(d, C-1), 203.9(s, C-2), 121.5 (d, C-3), 171.0(s, C-4), 55.3(d, C-5), 54.3(d, C-6), 48.9(d, G-7), 21.1 (t, C-8), 37.2(t, C-9), 56.5 (s, C-10), 80.5(s, C-11), 20.3(q, C-12), 22.9(q, C-13), 23.5(q, C-14), 24.1(q, G-15), 97.8(d, C-1glc), 71.6(d, C-2glc), 78.1(d, C-3glc), 74.7(d, C-4glc), 77.0(d, C-5glc), 62.8(t, C-6glc)。以上数据与文献[7]报道一致, 故确定化合物 **3**为半萜苷。

化合物 **4**(Vanillin)　$C_8H_8O_3$, 无色针状结晶, mp. 81~84 ℃, EI-MS m/z: 152 $[M]^+$; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 4.00(3H, s, -OCH_3), 7.45 (1H, s, H-2), 7.45(1H, d, J = 8.4 Hz, H-6), 7.06 (1H, d, J = 8.4 Hz, H-5), 9.85(1H, s, -CHO)。^{13}C NMR(CDCl$_3$, 100 MHz) δ 129.8(s, C-1), 108.8(d, C-2), 147.3(s, C-3), 151.79(s, C-4), 114.4(d, C-5), 127.5(d, C-6), 190.8(s, -CHO, CH), 56.1(q, -OCH_3, CH_3)。以上数据与文献[8]报道一致, 故确定化合物 **4**为香草醛。

化合物 **5**(**Daucosterol**)　白色无定形粉末, L-B反应阳性, Molish反应阳性。mp. 298~301 ℃。氢、碳谱等波谱数据与文献[9]对照, 确定化合物为胡萝卜苷。

化合物 **6**(**β-Sitosterol**)　白色针状结晶 (石油醚-乙酸乙酯), mp. 136~138 ℃。L-B反应呈阳性, H_2SO_4 显紫红色斑点, TLC 鉴定与 β-谷甾醇对照品在相同 R_f 值处呈现相同颜色斑点, 故确定该化合物为 β-谷甾醇。

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(C-9), 36.6 (C-10), 20.8 (C-11), 39.6 (C-12), 45.5 (C-13), 51.1 (C-14), 23.6 (C-15), 31.1 (C-16), 85.3 (C-17), 14.4 (C-18), 19.5 (C-19), 82.8 (C-20), 18.3 (C-21), 101.8 (C-1-can), 39.1 (C-2-can), 71.4 (C-3-can), 77.8 (C-4-can), 71.5 (C-5-can), 17.5 (C-6-can). These data were identical with the reported data[7].

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