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诺丽青果化学成分研究

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摘要:干燥诺丽青果粉末 95%乙醇提取物的正丁醇萃取部分经硅胶、Sephadex LH-20和 LiChroprep RP-18等材料分离,波谱学方法鉴定了 8个化合物,分别为乌苏酸(1)、6,7-二羟基香豆素(2)、胡萝卜甙(3)、车叶草甙(4)、Borreriagenin(5)、去乙酰车叶草甙(6)、O-*D*-glucopyranoside scopolin(7)、车叶草酸(8)。其中化合物 7为首次从该种中分到。

关键词:诺丽青果;车叶草甙;O-*D*-glucopyranoside scopolin;车叶草酸

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Chemical Constituents of *Morinda citrifolia*

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Abstract: The chemical constituents of *Morinda citrifolia* were isolated by silica gel, RP-18, Sephadex LH-20 and their structures were elucidated by spectral methods. 8 compounds were isolated and identified as ursolic acid(1), Esculetin(2), daucosterol(3), asperuloside(4), borreiagenin(5), deacetylasperuloside(6), O-*D*-glucopyranoside scopolin(7) and asperulosidic acid(8). The compound(7) was firstly isolated from *Morinda citrifolia*.

Key words: *Morinda citrifolia*; Asperuloside; O-*D*-glucopyranoside scopolin; Asperulosidic acid

诺丽(Noni)属茜草科巴戟天属(*Morinda L.*)植物,学名海巴戟(*Morinda citrifolia*),又名海巴戟天、四季果、印度桑葚等,我国主要分布于西南部到东南部、以及台湾和香港地区;Noni在南太平洋一带素有“仙果”之美称,作为保健及药用饮料已有上千年历史,其果实、叶子、枝干、根部均可入药;目前市场对 Noni产品需求以每年约 50%速度增加,是全球最畅销的健康产品之一^[1,2]。目前国外文献报道从诺丽中共分离鉴定出 160多个化合物,主要为环烯醚萜、蒽醌、木脂素、香豆素、三萜、甾醇、黄酮及其甙和苯醚类化合物等^[3,4]。但国内未见其研究报道,利用常规分离手段从诺丽青果乙醇提取物的正丁醇萃取部分共分离鉴定了 8个化合物,分别是:乌苏酸(1)、6,7-二羟基香豆素(2)、胡萝卜甙(3)、车叶草甙(4)、Borreriagenin(5)、去乙酰车叶草甙(6)、O-*D*-glucopyranoside scopolin(7)、车叶草酸(8),其中

化合物 7为首次从该种中分到。

1 材料与仪器

诺丽青果(*Morinda citrifolia*)由台湾谢氏公司提供。四川大学科学仪器厂生产的 XRC-1型显微熔点仪,温度计未校正;Bruker AM-400 和 Bruker-DRX-500 核磁共振仪,TMS为内标;VG Auto Spec-3000 和 APIQSTAR Pulsar 1 质谱仪;薄层层析硅胶和柱层析硅胶均为青岛海洋化工厂产品;LiChroprep RP-18 和 Sephadex LH-20 为 Merk 产品。显色方法为 254、365 nm 荧光、10%硫酸乙醇溶液和硫酸香草醛处理后加热显色、硫酸铜丙酮显色及碘蒸气显色。

2 提取与分离

干燥诺丽青果粉末用 95%工业乙醇室温提取四次(每次 2 d)得 436 g 浸膏。浸膏用水分散,分别用石油醚、乙酸乙酯、正丁醇萃取,合并正丁醇部分,减压浓缩得 45 g。正丁醇部分上硅胶柱分离,以氯仿-甲醇梯度洗脱得 14组分,组分 经反复柱层析、Sephadex LH-20(甲醇 氯仿 1:1洗脱)分离得化合

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物 2(50 mg);组分 V 经反复柱层析、制备 TLC 和 Sephadex LH-20得化合物 2(5 mg)和 3(15 mg);组分 V II经反复柱层析、Sephadex LH-20和重结晶得化合物 5(45 mg)和 7(80 mg);组分 X经反复柱层析、Sephadex LH-20和 RP-18层析得化合物 4(250 mg)和 6(20 mg);组分 X经反复柱层析、RP-18层析得化合物 8(1.5 g)。

3 结构鉴定

乌苏酸 (Ursolic acid, 1) 白色粉末, $C_{30}H_{48}O_4$, mp. 258 ~ 260 ; EIMS m/z : 456 [M]⁺, 423, 410, 248, 207, 203, 189; ¹H NMR (400 MHz, Pyridine) : 5.48 (1H, t, J = 3.2 Hz, H-12), 3.44 (1H, m, H-3), 2.18 (1H, d, J = 15.2 Hz, H-19), 1.23 (3H, s, CH₃), 1.23 (3H, s, CH₃), 1.02 (3H, d, J = 6.2 Hz, CH₃), 0.99 (3H, s, CH₃), 0.96 (3H, d, J = 5.2 Hz, CH₃), 0.88 (3H, s, CH₃), 0.87 (3H, s, CH₃); ¹³C NMR (100 MHz, Pyridine) : 179.9 (C-28), 139.3 (C-13), 125.7 (C-12), 78.2 (C-3), 55.9 (C-5), 53.6 (C-18), 48.1 (C-17), 48.1 (C-9), 42.5 (C-14), 40.0 (C-19), 39.6 (C-20), 39.5 (C-1), 39.4 (C-8), 39.2 (C-4), 37.5 (C-10), 37.3 (C-22), 33.6 (C-7), 31.8 (C-21), 28.9 (C-15), 28.8 (C-23), 28.2 (C-2), 25.0 (C-27), 24.0 (C-16), 23.7 (C-29), 21.5 (C-30), 18.9 (C-6), 17.6 (C-26), 17.5 (C-11), 16.7 (C-25), 15.8 (C-24)。以上数据与文献^[5]值相符。

6,7-二羟基香豆素 (Esculetin, 2) 无色针晶, $C_9H_6O_4$, mp. 267 ~ 269 ; FAB⁻MS m/z (%): 177 ([M-1], 100); ¹H NMR (400 MHz, MeOD) : 7.73 (1H, d, J = 9.5 Hz, H-4), 6.90 (1H, s, H-5), 6.74 (1H, s, H-8), 6.16 (1H, d, J = 9.5 Hz, H-3); ¹³C NMR (100 MHz, CDCl₃) : 164.2 (C-2), 151.7 (C-7), 150.2 (C-9), 145.8 (C-4), 144.2 (C-6), 112.8 (C-5), 112.5 (C-3), 112.3 (C-10), 103.5 (C-8)。以上数据与文献^[6]值相符。

胡萝卜甙 (Daucosterol, 3) 白色针晶, mp. 290 ~ 292 , 易溶于吡啶, 难溶于一般有机溶剂。Liebermann-Burchard 反应呈阳性, 与胡萝卜甙对照品共薄层, R_f 值和斑点颜色均一致。

车叶草甙 (asperuloside, 4) 白色晶体, $C_{18}H_{22}O_{11}$, mp. 125 ~ 127 ; ESI⁺MS m/z (%): 437 ([M + Na]⁺, 100); ¹H NMR (400 MHz, CD₃OD) : 7.29

(1H, d, J = 2.0 Hz, H-3), 5.92 (1H, d, J = 1.2 Hz, H-1), 5.74 (1H, s, H-7), 5.56 (1H, d, J = 7.2 Hz, H-6), 4.79 (1H, d, J = 1.2 Hz, H-1), 4.76 (1H, d, J = 14.0 Hz, H-10a), 4.68 (1H, d, J = 7.6 Hz, H-10b), 3.92 (1H, dd, J = 2.0, 12.0 Hz, H-6 a), 3.75~3.68 (2H, m, H-6 b, 5), 3.42~3.23 (5H, m, H-3, 5, 4, 9, 2), 2.10 (3H, s, CH₃COO); ¹³C NMR (100 MHz, CD₃OD) : 171.8 (CH₃CO), 171.7 (C-II), 149.7 (C-3), 143.0 (C-8), 128.7 (C-7), 105.1 (C-4), 99.1 (C-1), 92.4 (C-1), 85.5 (C-6), 77.3 (C-5), 77.0 (C-3), 73.7 (C-2), 70.6 (C-4), 62.1 (C-6), 61.2 (C-10), 44.5 (C-9), 36.6 (C-5), 20.8 (CH₃CO)。以上数据与文献^[7]值相符。

Borreriagenin (5) $C_{10}H_{15}O_5$, ¹H NMR (400 MHz, CD₃OD) : 5.77 (1H, br, s, H-7), 5.33 (1H, d, J = 7.6 Hz, H-6), 4.24 (1H, m, H-10), 4.18 (1H, m, H-10), 3.85 (1H, m, H-3), 3.81 (1H, m, H-3), 3.77 (1H, m, H-1), 3.72 (1H, m, H-1), 3.34 (1H, m, H-5), 3.09 (1H, m, H-9), 2.92 (1H, m, H-4); ¹³C NMR (100 MHz, CD₃OD) : 178.5 (C-11), 152.7 (C-8), 124.6 (C-7), 86.6 (C-6), 62.6 (C-3), 60.6 (C-1), 60.2 (C-10), 49.7 (C-9), 44.6 (C-4), 43.5 (C-5)。以上数据与文献^[8]值相符。

去乙酰车叶草甙 (Deacetylasperulobside, 6) 白色粉末, $C_{16}H_{20}O_{10}$, ESI⁺MS m/z (%): 437 ([M + Na]⁺, 100); ¹H NMR (400 MHz, CD₃OD) : 7.29 (1H, d, J = 2.0 Hz, H-3), 5.95 (1H, d, J = 1.2 Hz, H-1), 5.64 (1H, s, H-3), 5.57 (1H, m, H-6), 4.68 (1H, d, J = 8.0 Hz, H-1), 4.19 (2H, s, J = 14.0 Hz, H-10), 3.90 (1H, dd, J = 2.0, 12.0 Hz, H-6 a), 3.69~3.64 (2H, m, H-6 b, 5), 3.42~3.23 (5H, m, H-3, 5, 4, 9, 2); ¹³C NMR (100 MHz, CD₃OD) : 172.8 (C-II), 150.2 (C-3), 149.7 (C-8), 125.6 (C-7), 106.4 (C-4), 99.8 (C-1), 93.4 (C-1), 86.6 (C-6), 78.3 (C-5), 77.8 (C-3), 74.6 (C-2), 71.5 (C-4), 62.7 (C-6), 60.0 (C-10), 44.9 (C-9), 37.4 (C-5)。以上数据与文献^[7]值相符。

O- D-glucopyranoside scopolin (7) 白色晶体, $C_{16}H_{18}O_9$, mp. 217 ~ 219 , ¹H NMR (400 MHz, MeOD) : 7.81 (1H, d, J = 9.6 Hz, H-4), 7.14 (1H, s, H-5), 7.07 (1H, s, H-8), 6.21 (1H, d, J = 9.6 Hz, H-3), 5.01 (1H, d, J = 7.5 Hz, H-1), 3.79 (3H, s, OCH₃), 3.74 (1H, dd, J = 1.6, 11.6 Hz, H-6), 3.51

(1H, m, H-6), 3.41 (1H, m, H-3), 3.26 (3H, m, H-2, 4, 5); ^{13}C NMR (100 MHz, CDCl_3) : 162.4 (C-2), 151.5 (C-7), 150.5 (C-9), 147.8 (C-4), 145.4 (C-6), 114.7 (C-10), 114.1 (C-5), 110.9 (C-3), 104.7 (C-8), 101.5 (C-1), 78.5 (C-5), 78.0 (C-3), 74.6 (C-2), 71.1 (C-4), 62.2 (C-6), 57.2 (OCH_3)。以上数据与文献^[6]值相符。

车叶草酸 (Asperulosidic acid, 8) 白色粉末, $\text{C}_{18}\text{H}_{24}\text{O}_{12}$, ^1H NMR (400 MHz, CD_3OD) : 7.64 (1H, s, H-3), 6.01 (1H, s, H-7), 5.05 (1H, d, $J = 8.0$ Hz, H-1), 4.94 (1H, d, $J = 9.2$ Hz, H-10), 4.82 (1H, d, $J = 6.0$ Hz, H-6), 4.78 (1H, d, $J = 9.2$ Hz, H-10), 4.72 (1H, d, $J = 7.5$ Hz, H-1), 3.84 (1H, dd, $J = 2.0, 12.0$ Hz, H-6), 3.62 (1H, dd, $J = 2.0, 12.0$ Hz, H-6), 3.36 (1H, t, $J = 8.5$ Hz, H-3), 3.26 (3H, m, H-2~4~5), 3.21 (1H, t, $J = 7.0$ Hz, H-5), 2.62 (1H, t, $J = 8.0$ Hz, H-9), 2.08 (3H, s, Ac); ^{13}C NMR (100 MHz, CD_3OD) : 172.5 (CH_3CO), 170.9 (C-11), 155.2 (C-3), 145.9 (C-8), 131.8 (C-7), 108.5 (C-4), 101.2 (C-1), 100.5 (C-1), 78.5 (C-5), 77.8 (C-3), 75.3 (C-6), 74.9 (C-2), 71.5 (C-4), 63.7 (C-10), 62.9 (C-6), 46.2 (C-9), 42.4 (C-5), 20.7 (CH_3CO)。以上数据与文献^[9]值相符。

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