

香瓜茄的化学成分分析

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[摘要] 目的:对茄科 Solanaceae 植物甘肃武威香瓜茄 *Solanum muicatum* 成熟果实的化学成分进行分离纯化研究,并对分离得到的化合物进行化学成分鉴定。方法:采用95%的乙醇对香瓜茄干果进行加热提取,并依次用石油醚、乙酸乙酯、正丁醇进行萃取,然后采用薄层色谱法,正相硅胶柱色谱法, LH-20 羟丙基葡聚糖凝胶色谱法和制备高效液相色谱法等方法对香瓜茄95%乙醇提取物的乙酸乙酯萃取部位进行分离纯化,并依据化合物的理化性质并通过核磁共振、质谱等现代波谱技术对化合物的化学结构进行鉴定。结果:最终从香瓜茄中分离纯化得到7个化合物,其中3个生物碱皂苷类化合物,2个黄酮类化合物及2个有机酸类化合物,分别鉴定为澳洲茄碱(solasonine 1),澳洲茄边碱(solamargine 2),澳洲茄胺(solasodine 3),槲皮素(quercetin 4),柚皮素(naringenin 5),阿魏酸(ferulic acid 6),熊果酸(ursone 7)。结论:以上7种化合物均为首次从该植物果实中分离纯化得到,该研究为综合开发及寻找天然植物性抗炎、抗肿瘤活性物质提供一定的化学依据和基础。

[关键词] 香瓜茄; 成熟果实; 核磁共振; 化学成分

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Chemical Constituents from Mature Fruits of *Solanum muicatum*

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[Abstract] **Objective:** To study the chemical constituents from the mature fruits of *Solanum muicatum*.

Method: *S. muicatum* dry fruits were heated and extracted by using 95% ethanol, and then were extracted with petroleum ether, ethyl acetate and *n*-butanol in turn. Ethyl acetate extract fraction of *S. muicatum* 95% ethanol extract was isolated and purified by using chromatography on silica gel, Sephadex LH-20 column chromatography and preparative HPLC methods. The structures of the compounds were then identified by analysis of NMR and spectroscopic data by comparison with those reported on the literature. **Result:** Seven compounds were isolated from 95% ethanol and they were identified as solasonine (1), solamargine (2), solasodine (3), quercetin (4),

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naringenin (5), ferulic acid (6), and ursone (7). **Conclusion:** All of the compounds were obtained from this plant for the first time, providing certain chemical basis and foundation for the comprehensive development and the search for natural plant anti-inflammatory and antitumor active substances

[**Key words**] *Solanum muicatum*; mature fruits; nuclear magnetic resonance; chemical constituents

香瓜茄形似心脏,原产于南美的安第斯山北麓^[1],又名人参果,香瓜梨、艳果、香艳茄、香艳梨、茄瓜、甜茄等,果实呈梨状、椭圆形、乳黄色浆果,果实皮薄、肉厚且多汁,成熟时果皮呈淡绿色至黄色,并常带有紫色或紫红色条纹^[2]。我国华南植物园 1985 年 9 月首次从新西兰引入,近年来多以译名“香瓜茄”出现于市面^[3]。果实营养价值高,果肉爽甜多汁、清香味美,可溶性固形物质量分数 10%,含有丰富的维生素 C 和多种微量元素,可食率 95% 以上^[4]。每 100 g 香瓜茄鲜果中含钙量高达 910 mg,是番茄的 114 倍。并能预防高血压、肥胖病、冠心病、癌症,曾被医学界称之为“生命之火”、“抗癌之王”^[5]。据文献报道,香瓜茄化学成分具有抗肿瘤^[6]、抗炎^[7]、抗菌^[8]、抗氧化^[9]等方面的药理作用。目前对香瓜茄的化学成分研究报道较少。为了进一步深入研究香瓜茄提取物的活性成分,阐明其物质基础,本课题组通过正相硅胶, LH-20 羟丙基葡聚糖凝胶 (Sephadex LH-20) 等柱色谱法及制备液相色谱法对香瓜茄中的活性物质进行了系统的分离纯化,并从中分离得到 7 个化合物。通过波谱分析鉴定其结构为澳洲茄碱(1),澳洲茄边碱(2),澳洲茄胺(3),槲皮素(4),柚皮素(5),阿魏酸(6),熊果酸(7)。这 7 种化合物均为首次从该属植物中分离得到。据文献报道^[10-13],澳洲茄碱、澳洲茄边碱、澳洲茄胺均可从同科植物龙葵中分离纯化得到;槲皮素、柚皮素均可从茄科植物疏刺茄中分离纯化得到;阿魏酸可从同科植物锦灯笼根茎中分离纯化得到;熊果酸可从茄科植物马尿泡中分离纯化得到。

1 材料

Avance III-500 MHz 型核磁共振仪(德国 Bruker 公司), AB 5600 + Q TOF 型高分辨质谱仪(美国 AB Sciex 公司); P270 型制备型高效液相色谱仪(大连依利特分析仪器有限公司), 旋转蒸发仪(上海亚荣生化仪器厂); LH-20 羟甲基葡聚糖凝胶 (Sephadex LH-20, 美国 Pharmacia 公司), 柱色谱硅胶(200 ~ 300 目, 青岛海洋化工有限公司); 乙腈为色谱纯(德国 Merck 公司), 其他试剂均为分析纯(国药集团化学试剂有限公司)。

香瓜茄鲜果(购自甘肃武威市), 经上海市农业

科学院唐庆九研究员鉴定为茄科茄属植物香瓜茄 *Solanum muicatum* 的成熟果实。

2 提取分离

取香瓜茄鲜果 800 kg, 清水洗净, 晾干, 切成约 5 mm 薄片, 50 °C 烘干至恒重, 粉碎后, 用 95% 乙醇回流提取 3 次, 每次 2 ~ 3 h, 合并提取液, 减压浓缩至无乙醇味后, 加适量蒸馏水分散, 依次用石油醚、乙酸乙酯、正丁醇萃取, 减压浓缩后得石油醚萃取物 1 600 g, 乙酸乙酯萃取物 2 300 g, 正丁醇萃取物 2 670 g。

乙酸乙酯萃取部分经正相硅胶柱色谱, 以石油醚-乙酸乙酯(100:1~0:100)进行梯度洗脱, 经 TLC 检测合并相同组分得 10 个流分(A1~A10), 其中 A3 流分经 Sephadex LH-20 色谱柱反复纯化得化合物 6(18 mg)。A1 流分经硅胶色谱柱石油醚-乙酸乙酯(50:1~0:1)梯度洗脱得到 6 个亚组分(A1.1~A1.6), 亚组分 A1.3 经 Sephadex LH-20 色谱柱反复纯化得化合物 7(33 mg)。亚组分 A1.5 再上硅胶柱, 以三氯甲烷-甲醇(20:80~40:60)梯度洗脱, 经 TLC 检测合并相同组分得 B1~B5, 流分 B3 经制备 HPLC 以乙腈-水(60:40~70:30)梯度洗脱得化合物 4(56 mg), 流分 B5 经制备 HPLC 以乙腈-水(60:40~70:30)梯度洗脱得化合物 5(24 mg)。A7 流分经制备 HPLC 以乙腈-水(60:40~80:20)梯度洗脱得亚组分 A7.1~A7.5, 亚组份 A7.4 再经制备 HPLC 以乙腈-水(60:40~70:30)梯度洗脱得化合物 1(19 mg), 化合物 2(15 mg) 和化合物 3(13 mg)。分离流程见图 1, 各化合物结构见图 2。

3 结构鉴定

化合物 1 白色粉末; MS m/z 883 [M + H]⁺。¹H-NMR (CD₃OD, 500 MHz) δ : 1.73 (1H, m, H-1), 0.99 (1H, s, H-1), 2.66 (1H, m, H-2), 1.89 (1H, m, H-2), 4.10 (1H, m, H-3), 2.55 (1H, m, H-3), 2.53 (1H, m, H-4), 5.37 (1H, m, H-6), 1.91 (1H, m, H-7), 1.50 (1H, m, H-8), 1.51 (1H, m, H-8), 0.89 (1H, m, H-9), 1.39 (1H, m, H-11), 1.47 (1H, m, H-11), 1.71 (1H, m, H-12), 1.09 (1H, m, H-12), 1.09 (1H, m, H-14), 2.51 (1H, m, H-14), 1.57 (1H, m, H-15), 4.51 (1H, m, H-16), 1.78

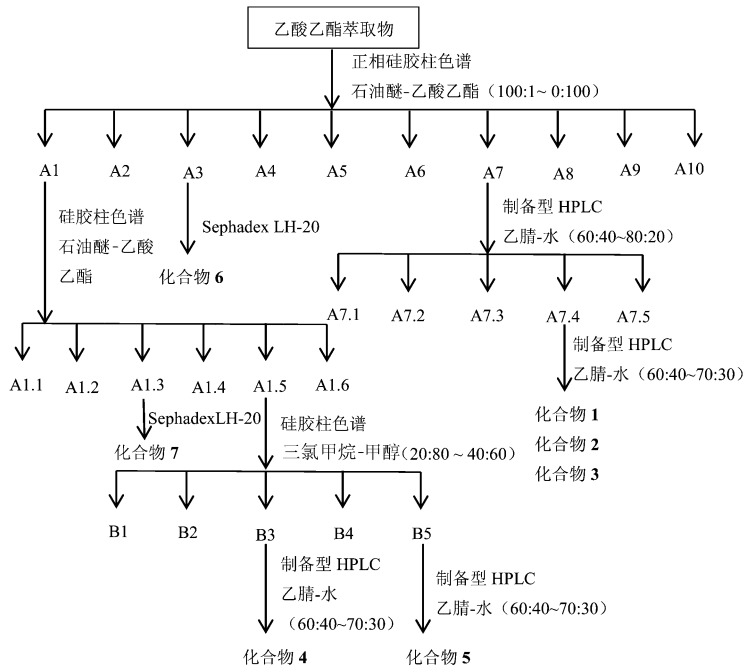


图 1 乙酸乙酯萃取部位分离纯化流程

Fig. 1 Separated and purified flowchart of ethyl acetate extract

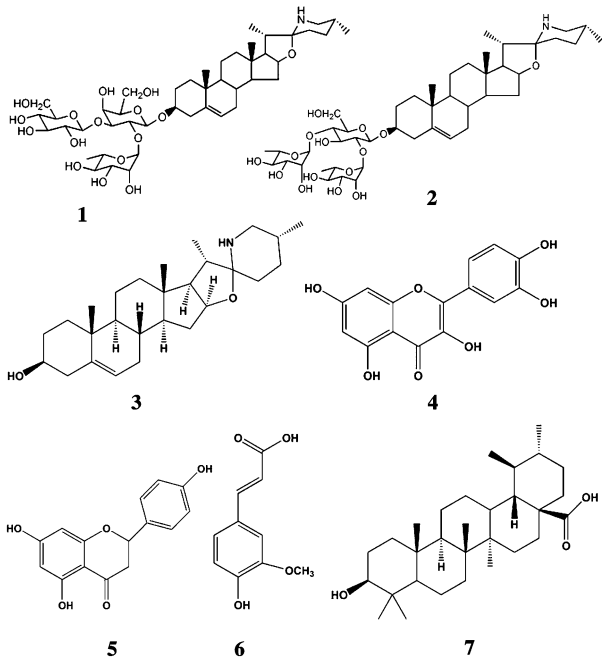


图 2 化合物 1~7 结构

Fig. 2 Structure of compounds 1-7

(1H, m, H-17), 0.88 (3H, s, CH₃-18), 0.90 (3H, s, CH₃-19), 2.19 (1H, m, H-20), 1.00 (3H, d, J = 7.11 Hz, CH₃-21), 1.71 (1H, m, H-23), 1.72 (1H, m, H-23), 1.61 (1H, m, H-24), 1.67 (1H, m, H-24), 1.31 (1H, m, H-25), 2.51 (1H, m, H-25), 2.50 (1H, m, H-26), 0.80 (3H, d, J = 5.91 Hz, CH₃-27), 4.99 (1H, d, J = 8.06 Hz, H-1'), 3.71 (1H, m, H-

2'), 4.29 (1H, m, H-3'), 5.07 (1H, m, H-4'), 4.28 (1H, m, H-5'), 4.25 (1H, m, H-6'), 4.22 (1H, m, H-6'), 6.47 (1H, s, H-1''), 4.90 (1H, m, H-2''), 4.58 (1H, m, H-3''), 4.46 (1H, m, H-4''), 4.96 (1H, m, H-5''), 1.59 (1H, d, J = 5.61 Hz, H-6''), 5.09 (1H, d, J = 8.13 Hz, H-1'''), 4.58 (1H, m, H-2'''), 4.25 (1H, m, H-3'''), 4.11 (1H, m, H-4'''), 4.00 (1H, m, H-5'''), 4.55 (1H, m, H-6'''), 4.32 (1H, m, H-6'''); ¹³C-NMR (CD₃OD, 126 MHz) δ: 38.1 (C-1), 35.0 (C-2), 75.3 (C-3), 41.7 (C-4), 140.0 (C-5), 121.5 (C-6), 35.4 (C-7), 32.3 (C-8), 50.9 (C-9), 37.2 (C-10), 20.0 (C-11), 40.1 (C-12), 40.5 (C-13), 56.0 (C-14), 34.1 (C-15), 79.0 (C-16), 64.3 (C-17), 16.5 (C-18), 19.3 (C-19), 41.4 (C-20), 15.6 (C-21), 97.8 (C-22), 34.6 (C-23), 30.9 (C-24), 32.9 (C-25), 48.0 (C-26), 19.5 (C-27), 99.9 (C-1'), 75.1 (C-2'), 84.5 (C-3'), 69.3 (C-4'), 74.6 (C-5'), 62.1 (C-6'), 102.3 (C-1''), 72.7 (C-2''), 73.4 (C-3''), 74.3 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 105.0 (C-1'''), 74.4 (C-2'''), 77.2 (C-3'''), 71.3 (C-4'''), 78.2 (C-5'''), 61.5 (C-6'''). 以上数据与文献[14]对照, 鉴定为澳洲茄碱。

化合物 2 白色粉末; Liebermann-Burchard 反应阳性; MS *m/z* 868.4 [M + H]⁺。¹H-NMR (CD₃OD, 500 MHz) δ: 1.74 (1H, m, H-1), 1.00

(1H, m, H-1), 1.89 (1H, m, H-2), 1.98 (1H, m, H-2), 3.50 (1H, m, H-3), 2.73 (1H, m, H-4), 2.70 (1H, m, H-4), 5.32 (1H, m, H-6), 1.46 (1H, m, H-7), 2.00 (1H, m, H-7), 1.56 (1H, m, H-8), 0.88 (1H, m, H-9), 1.40 (1H, m, H-11), 1.49 (1H, m, H-11), 1.12 (1H, m, H-12), 1.70 (1H, m, H-12), 1.02 (1H, m, H-14), 1.75 (1H, m, H-14), 1.41 (1H, m, H-15), 1.41 (1H, m, H-15), 4.40 (1H, m, H-16), 1.69 (1H, m, H-17), 0.87 (3H, s, CH₃-18), 1.05 (3H, s, CH₃-19), 1.93 (1H, m, H-20), 1.03 (3H, d, *J* = 6.94 Hz, CH₃-21), 1.69 (1H, m, H-23), 1.70 (1H, m, H-23), 1.63 (1H, m, H-24), 1.58 (1H, m, H-25), 1.37 (1H, m, H-25), 2.52 (1H, m, H-26), 0.85 (3H, d, *J* = 5.98 Hz, CH₃-27), 4.60 (1H, m, H-1'), 4.30 (1H, m, H-2'), 4.26 (1H, m, H-3'), 4.40 (1H, m, H-4'), 3.51 (1H, m, H-5'), 4.20 (1H, m, H-6'), 4.21 (1H, m, H-6'), 6.48 (1H, m, H-1''), 4.71 (1H, m, H-2''), 4.62 (1H, m, H-3''), 4.40 (1H, m, H-4''), 4.98 (1H, m, H-5''), 1.57 (1H, m, H-6''), 5.48 (1H, m, H-1'''), 4.70 (1H, m, H-2'''), 4.57 (1H, m, H-3'''), 4.22 (1H, m, H-4'''), 5.06 (1H, m, H-5'''), 1.68 (1H, d, *J* = 6.09 Hz, H-6'''); ¹³C-NMR (CD₃OD, 126 MHz) δ: 38.7 (C-1), 31.2 (C-2), 76.3 (C-3), 40.9 (C-4), 140.7 (C-5), 121.6 (C-6), 35.7 (C-7), 32.2 (C-8), 50.1 (C-9), 38.7 (C-10), 20.0 (C-11), 39.8 (C-12), 40.0 (C-13), 56.8 (C-14), 35.7 (C-15), 80.1 (C-16), 63.8 (C-17), 16.7 (C-18), 19.2 (C-19), 41.0 (C-20), 15.8 (C-21), 97.9 (C-22), 35.9 (C-23), 31.2 (C-24), 32.2 (C-25), 50.1 (C-26), 19.3 (C-27), 100.0 (C-1'), 78.3 (C-2'), 72.3 (C-3'), 77.2 (C-4'), 76.3 (C-5'), 62.8 (C-6'), 102.0 (C-1''), 72.4 (C-2''), 72.4 (C-3''), 73.4 (C-4''), 70.9 (C-5''), 18.3 (C-6''), 101.6 (C-1'''), 72.5 (C-2'''), 72.4 (C-3'''), 73.4 (C-4'''), 70.5 (C-5'''), 18.2 (C-6'''). 以上数据与文献[15]对照, 鉴定为澳洲茄边碱。

化合物 3 白色粉末; MS *m/z* 414.6 [M + H]⁺. ¹H-NMR (CD₃OD, 500 MHz) δ: 0.98 (1H, m, H-1), 1.75 (1H, m, H-1), 1.77 (1H, m, H-2), 1.40 (1H, m, H-2), 3.59 (1H, m, H-3), 2.23 (1H, m, H-4), 2.27 (1H, m, H-4), 5.30 (1H, m, H-6), 1.48 (1H, m, H-7), 1.99 (1H, m, H-7), 1.61 (1H, m, H-8), 0.82 (1H, d, *J* = 6.01 Hz, H-9), 1.51 (1H, m, H-11), 1.39 (1H, m, H-11), 1.01 (1H, m, H-12), 1.59

(1H, m, H-12), 0.93 (1H, m, H-14), 1.88 (1H, m, H-15), 1.22 (1H, m, H-12), 4.32 (1H, m, H-16), 1.65 (1H, m, H-17), 0.84 (3H, s, H-18), 0.87 (1H, s, H-19), 1.85 (1H, m, H-20), 0.87 (3H, d, *J* = 6.09 Hz, H-21), 1.56 (1H, m, H-23), 1.50 (1H, m, H-24), 1.33 (1H, m, H-24), 1.53 (1H, m, H-25), 2.60 (1H, m, H-26), 2.67 (1H, m, H-26), 0.88 (3H, d, *J* = 6.0 Hz, H-27); ¹³C-NMR (CD₃OD, 126 MHz) δ: 38.5 (C-1), 30.2 (C-2), 76.0 (C-3), 40.1 (C-4), 140.0 (C-5), 121.2 (C-6), 35.1 (C-7), 32.0 (C-8), 49.9 (C-9), 38.5 (C-10), 20.0 (C-11), 39.2 (C-12), 40.5 (C-13), 57.3 (C-14), 35.2 (C-15), 81.5 (C-16), 62.3 (C-17), 16.0 (C-18), 18.1 (C-19), 41.1 (C-20), 16.8 (C-21), 96.9 (C-22), 36.9 (C-23), 32.7 (C-24), 33.9 (C-25), 53.5 (C-26), 19.7 (C-27)。以上数据与文献[16]对照, 鉴定为澳洲茄胺。

化合物 4 黄色粉末(乙醇); 紫外灯下呈现黄绿色荧光, HCl-Mg 反应为阳性; ¹H-NMR (DMSO-*d*₆, 500 MHz) δ: 6.17 (1H, d, *J* = 2.01 Hz, H-6), 6.39 (1H, d, *J* = 2.03 Hz, H-8), 6.86 (1H, d, *J* = 8.16 Hz, H-5'), 7.66 (1H, d, *J* = 3.12 Hz, H-2'), 7.55 (1H, d, *J* = 2.55 Hz, H-6'); ¹³C-NMR (DMSO-*d*₆, 126 MHz) δ: 146.8 (C-2), 135.0 (C-3), 175.8 (C-4), 158.9 (C-5), 95.2 (C-6), 163.8 (C-7), 93.6 (C-8), 156.3 (C-9), 103.1 (C-10), 122.8 (C-1'), 115.5 (C-5'), 120.0 (C-6')。以上数据与文献[17]对照, 鉴定为槲皮素。

化合物 5 淡黄色粉末(乙醇); HCl-Mg 反应呈紫红色; ¹H-NMR (DMSO-*d*₆, 500 MHz) δ: 5.90 (2H, s, H-6, 8), 3.22 (1H, dd, H-3a), 5.45 (1H, dd, *J* = 3.05, 12.81 Hz, H-2), 6.80 (2H, d, *J* = 8.52 Hz, H-3', 5'), 2.80 (1H, dd, *J* = 12.8, 17.1 Hz, H-3b), 5.42 (1H, dd, *J* = 3.11, 12.80 Hz, H-2), 7.32 (2H, d, *J* = 8.17 Hz, H-2', 6'), 12.12 (1H, s, 5-OH), 9.56 (1H, s, 4'-OH), 10.05 (1H, s, 7-OH); ¹³C-NMR (DMSO-*d*₆, 126 MHz) δ: 79.6 (C-2), 42.9 (C-3), 162 (C-4), 164.2 (C-5), 96.6 (C-6), 166.9 (C-7), 95.8 (C-8), 164 (C-9), 102.2 (C-10), 131.2 (C-1'), 128.8 (C-2', 6')。以上数据与文献[18]对照, 鉴定为柚皮素。

化合物 6 无色针状结晶(甲醇-水); MS *m/z* 194 [M + H]⁺; ¹H-NMR (DMSO-*d*₆, 500 MHz) δ: 7.20 (1H, d, *J* = 1.6 Hz, H-2), 6.85 (1H, d, *J* = 8.0

Hz, H-5), 7.15 (1H, dd, $J = 1.8, 7.5$ Hz, H-6), 7.55 (1H, d, $J = 16.11$ Hz, H-7), 6.40 (1H, d, $J = 16.12$ Hz, H-8), 9.60 (1H, s, 4'-OH), 12.05 (1H, s, 9-COOH), 3.75 (3H, s, OCH₃); ¹³C-NMR (DMSO-*d*₆, 126 MHz) δ : 127.1 (C-1), 115.5 (C-2), 149.0 (C-3), 146.9 (C-4), 116.2 (C-5), 122.6 (C-6), 146.5 (C-7), 110.6 (C-8), 169.2 (C-9), 58.5 (OCH₃)。以上数据与文献[19]对照, 鉴定为阿魏酸。

化合物7 白色粉末(三氯甲烷); MS m/z 457 [M + H]⁺; ¹H-NMR (DMSO-*d*₆, 500 MHz) δ : 0.98 (3H, s, H-30), 1.02 (6H, s, H-27, 29), 1.05 (3H, s, H-26), 0.80 (3H, s, H-25), 0.86 (3H, s, H-24), 2.15 (1H, d, H-18), 5.40 (1H, s, H-12), 3.44 (1H, m, H-3); ¹³C-NMR (DMSO-*d*₆, 126 MHz) δ : 39.1 (C-1), 26.8 (C-2), 77.6 (C-3), 38.8 (C-4), 53.9 (C-5), 18.2 (C-6), 33.1 (C-7), 40.6 (C-8), 47.6 (C-9), 37.9 (C-10), 23.0 (C-11), 125.2 (C-12), 138.5 (C-13), 41.9 (C-14), 27.9 (C-15), 23.9 (C-16), 46.9 (C-17), 53.2 (C-18), 39.2 (C-19), 38.9 (C-20), 30.5 (C-21), 37.1 (C-22), 27.9 (C-23), 15.6 (C-24), 15.7 (C-25), 17.1 (C-26), 23.5 (C-27), 179.1 (C-28), 16.8 (C-29), 21.1 (C-30)。以上数据与文献[20]对照, 鉴定为熊果酸。

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