中华猕猴桃根的化学成分研究

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[摘要] 目的:研究中华猕猴桃 *Actinidia chinensis*根的化学成分。方法:中华猕猴桃根的 95%乙醇提取物,依次用石油醚、醋酸乙酯、正丁醇萃取,应用多种色谱技术对醋酸乙酯部分进行分离纯化,通过波谱数据分析 (MS, IR, ^{1}H-NMR, ^{13}C-NMR)进行结构鉴定。结果:从醋酸乙酯部分分离得到 7个化合物,经鉴定为 2α羟基齐墩果酸 (1), 2α羟基乌苏酸 (2), 蔷薇酸 (3), 23羟基乌苏酸 (4), 3β-O-乙酰乌苏果酸 (5), 麦角甾-4, 6, 8(14), 22-四烯-3-酮 (6), β谷甾醇 (7)。结论:所有化合物均为首次从该植物中分离鉴定。

[关键词] 中华猕猴桃;三萜;甾体
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中华猕猴桃 *Actinidia chinensis* Planch. 为猕猴桃科 Actinidiaceae猕猴桃属浆果类藤本果树,野生居群分布于秦岭、淮河以南的广大地区[1]。全株均可药用,其根、根皮性寒,味苦、涩,具有清热解毒、活血消肿、祛风利湿的功效,可用于治疗肝炎、水肿、风湿性关节炎、跌打损伤、痢疾、淋巴结结核、胃癌、乳腺癌等[2]。迄今为止,对其化学成分的报道较少。作者对中华猕猴桃根醋酸乙酯萃取部分的化学成分进行了研究,从中分离得到 5个三萜类化合物, 2个甾体类化合物,所有化合物均为从该植物中首次分离鉴定。

1 仪器与材料

VG Auto Spec 3000型质谱仪测定, EI-MS用 70ev电子轰击源。IR采用 KBr压片,由 Bio-Rad FTS-135分光光度计测定。^{1}H和 ^{13}C-NMR (DEPT)采用 Bruker AM 400或 DRX 500型核磁共振光谱仪,以 TMS为内标测定。柱色谱硅胶 (200～300目)和薄层色谱硅胶 GF254均为青岛海洋化工厂生产, C_8, C_{18}薄层板和柱色谱材料购自 Merck公司。

中华猕猴桃根于 2005年 4月采自贵州省凯里市,经中国科学院昆明植物研究所雷立公博士鉴定为猕猴桃科猕猴属植物中华猕猴桃 *A. chinensis*,标本存放于昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室。

2 提取分离

干燥的中华猕猴桃根 10 kg,粉碎后用 95%乙醇回流提取 3次,每次 2 h,滤液减压浓缩至浸膏。浸膏加水悬浮后,依次用石油醚、醋酸乙酯、正丁醇萃取,回收溶剂后分别得萃取物 30.0, 85.0, 101.5 g。醋酸乙酯部分 (80.0 g)经硅胶柱色谱,用氯仿-甲醇 (100∶0, 98∶2, 95∶5, 90∶10, 80∶20)梯度洗脱,得到 F_1～F_6共 6个组分。F_3组分经硅胶柱色谱,用石油醚-丙酮 (70∶30, 65∶35, 60∶40)梯度洗脱得到组分 1～5,第 2、3组分经 C_8和 C_{18}柱色谱,用甲醇-水 (80∶20)洗脱,分离得到化合物 **1** (15 mg), **2** (35 mg), **3** (7 mg), **4** (11 mg)。F_1组分经硅胶柱色谱,用氯仿-丙酮 (98∶2),石油醚-醋酸乙酯 (80∶20)混合溶剂系统反复色谱,分离得到化合物 **5** (38 mg), **6** (7 mg)和 **7** (662 mg)。

3 结构鉴定

化合物 **1** 白色无定型粉末 (氯仿-甲醇), IR (KBr) cm^{-1}: 3 426 (OH), 1 694 (C=O), 1 638 (C=C), 1 461, 1 387, 1 051; ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.93, 0.97, 0.99, 1.01, 1.07, 1.25, 1.27 (each

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3H, s, 7 ×CH_3), 3.29 (1H, dd, J = 11.4, 4.5 Hz, H-18), 3.40 (1H, d, J = 9.3 Hz, H-3), 4.10 (1H, td, J = 11.1, 4.1 Hz, H-2), 5.46 (1H, br s, H-12); ^{13}C-NMR (125 MHz, C_5D_5N) δ: 47.8 (C-1), 68.6 (C-2), 83.8 (C-3), 39.8 (C-4), 56.0 (C-5), 18.9 (C-6), 33.2 (C-7), 39.9 (C-8), 48.2 (C-9), 38.6 (C-10), 23.8 (C-11), 122.5 (C-12), 144.8 (C-13), 42.2 (C-14), 28.3 (C-15), 24.0 (C-16), 46.7 (C-17), 42.0 (C-18), 46.5 (C-19), 31.0 (C-20), 34.2 (C-21), 33.2 (C-22), 29.4 (C-23), 17.7 (C-24), 16.9 (C-25), 17.5 (C-26), 26.2 (C-27), 180.2 (C-28), 33.2 (C-29), 23.8 (C-30)。以上数据与文献 [3] 报道的 2α羟基齐墩果酸一致。

化合物 2 白色无定型粉末 (氯仿-甲醇), EI-MS m/z: 473 $[M+1]^+$ (1); IR (KBr) cm^{-1}: 3 427 (OH), 1 692 (C=O), 1 638 (C=C), 1 457, 1 389, 1 107, 1 049; ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.94 (3H, s, H-25), 0.97 (3H, d, J = 6.4 Hz, H-29), 0.99 (3H, d, J = 5.4 Hz, H-30), 1.03 (3H, s, H-24), 1.07 (3H, s, H-27), 1.20 (3H, s, H-26), 1.27 (3H, s, H-23), 2.61 (1H, d, J = 11.3 Hz, H-18), 3.40 (1H, d, J = 9.4 Hz, H-3), 4.09 (1H, td, J = 11.1, 4.3 Hz, H-2), 5.45 (1H, br s, H-12); ^{13}C-NMR (125 MHz, C_5D_5N) δ: 48.0 (C-1), 68.7 (C-2), 83.9 (C-3), 39.9 (C-4), 56.0 (C-5), 18.9 (C-6), 33.5 (C-7), 40.1 (C-8), 48.1 (C-9), 38.5 (C-10), 24.0 (C-11), 125.6 (C-12), 139.4 (C-13), 42.8 (C-14), 28.7 (C-15), 25.0 (C-16), 48.0 (C-17), 53.6 (C-18), 39.5 (C-19), 39.5 (C-20), 31.1 (C-21), 37.5 (C-22), 29.4 (C-23), 17.5 (C-24), 17.0 (C-25), 17.6 (C-26), 24.0 (C-27), 180.0 (C-28), 17.8 (C-29), 21.5 (C-30)。以上数据与文献 [4,5] 报道的 2α羟基乌苏酸基本一致。

化合物 3 白色无定型粉末 (氯仿-甲醇), EI-MS m/z: 488 $[M]^+$ (6); ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.89 (3H, s, H-24), 0.97 (3H, s, H-25), 1.10 (3H, s, H-26), 1.10 (3H, d, J = 6.5 Hz, H-30), 1.25 (3H, s, H-23), 1.40 (3H, s, H-29), 1.63 (3H, s, H-27), 3.03 (1H, s, H-18), 3.75 (1H, d, J = 2.0 Hz, H-3), 4.30 (1H, m, H-2), 5.57 (1H, br s, H-12); ^{13}C-NMR (125 MHz, C_5D_5N) δ: 42.4 (C-1), 66.1 (C-2), 79.4 (C-3), 38.7 (C-4), 48.8 (C-5), 18.6 (C-6), 33.6 (C-7), 40.6 (C-8), 47.7 (C-9), 38.8 (C-10), 24.1 (C-11), 128.0 (C-12), 140.0 (C-13), 42.9 (C-14), 29.3 (C-15), 27.0 (C-16), 48.3 (C-17), 54.6 (C-18), 72.7 (C-19), 42.2 (C-20), 27.1 (C-21), 38.8 (C-22), 29.5 (C-23), 22.3 (C-24), 16.8 (C-25), 17.3 (C-26), 24.7 (C-27), 180.7 (C-28), 27.1 (C-29), 16.7 (C-30)。以上数据与文献 [3] 报道的蔷薇酸一致。

化合物 4 白色无定型粉末 (氯仿-甲醇), IR (KBr) cm^{-1}: 3 421 (OH), 1 694 (C=O), 1 635 (C=C), 1 456, 1 387, 1 045; ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.92 (3H, d, J = 6.1 Hz, H-29), 0.96 (3H, d, J = 6.4 Hz, H-30), 0.95, 1.04, 1.06, 1.16 (each 3H, s, 4 ×CH_3), 2.62 (1H, d, J = 11.2 Hz, H-18), 3.72 (1H, d, J = 10.3 Hz, H-23a), 4.18 (1H, d, J = 10.7 Hz, H-23b), 4.22 (1H, m, H-3), 5.48 (1H, br s, H-12); ^{13}C-NMR (125 MHz, C_5D_5N) δ: 39.0 (C-1), 27.7 (C-2), 73.7 (C-3), 42.9 (C-4), 48.6 (C-5), 18.6 (C-6), 33.3 (C-7), 40.0 (C-8), 48.1 (C-9), 37.5 (C-10), 23.7 (C-11), 125.7 (C-12), 139.3 (C-13), 42.9 (C-14), 28.8 (C-15), 25.0 (C-16), 48.1 (C-17), 53.6 (C-18), 39.5 (C-19), 39.5 (C-20), 31.1 (C-21), 37.5 (C-22), 68.1 (C-23), 13.1 (C-24), 16.1 (C-25), 17.5 (C-26), 23.9 (C-27), 180.0 (C-28), 17.4 (C-29), 21.4 (C-30)。以上数据与文献 [6] 报道的 23羟基乌苏酸一致。

化合物 5 白色无定型粉末 (氯仿), EI-MS m/z: 499 $[M+H]^+$ (1); IR (KBr) cm^{-1}: 3 432 (OH), 1 736, 1 694 (C=O), 1 631 (C=C), 1 459, 1 370, 1 246; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.78 (3H, s, H-24), 0.85 (3H, s, H-25), 0.86 (3H, d, J = 8.1 Hz, H-29), 0.87 (3H, s, H-27), 0.95 (3H, d, J = 7.1 Hz, H-30), 0.96 (3H, s, H-26), 1.07 (3H, s, H-27), 2.05 (3H, s, OAc), 2.18 (1H, d, J = 11.2 Hz, H-18), 4.50 (1H, m, H-3), 5.24 (1H, br s, H-12); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 38.3 (C-1), 23.6 (C-2), 81.0 (C-3), 37.7 (C-4), 55.4 (C-5), 18.2 (C-6), 32.8 (C-7), 40.2 (C-8), 47.5 (C-9), 36.7 (C-10), 23.3 (C-11), 125.8 (C-12), 138.0 (C-13), 42.0 (C-14), 28.1 (C-15), 24.1 (C-16), 48.0 (C-17), 52.7 (C-18), 39.1 (C-19), 38.9 (C-20), 30.6 (C-21), 36.7 (C-22), 28.0 (C-23), 15.5 (C-24), 16.7 (C-25), 17.0 (C-26), 23.6 (C-27), 182.6 (C-28), 17.1 (C-29), 21.2

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(C-30), 171.0 ($COCH_3$), 21.3 ($COCH_3$)。以上数据与文献[5]报道的 3β-O-乙酰熊果酸基本一致。

化合物 6 淡黄色针状结晶(氯仿), EI-MS m/z: 268 [M - C_9H_{17}]$^+$ (36); IR (KBr) cm^{-1}: 1 659, 1 642, 1 586 (C=O), 973 (△^{22}-trans); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.83 (3H, d, J=7.1 Hz, H-26), 0.85 (3H, d, J=8.0 Hz, H-27), 0.93 (3H, d, J=6.8 Hz, H-28), 0.96 (3H, s, H-18), 1.00 (3H, s, H-19), 1.06 (3H, d, J=6.7 Hz, H-21), 5.24 (2H, m, H-22、23), 5.74 (1H, s, H-4), 6.03 (1H, d, J=9.5 Hz, H-6), 6.61 (1H, d, J=9.5 Hz, H-7); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 34.2 (C-1), 34.1 (C-2), 199.4 (C-3), 123.0 (C-4), 164.3 (C-5), 124.5 (C-6), 133.9 (C-7), 124.5 (C-8), 44.4 (C-9), 36.8 (C-10), 20.0 (C-11), 35.7 (C-12), 44.0 (C-13), 156.0 (C-14), 25.4 (C-15), 27.7 (C-16), 55.8 (C-17), 19.0 (C-18), 16.7 (C-19), 39.2 (C-20), 21.2 (C-21), 135.0 (C-22), 132.6 (C-23), 42.9 (C-24), 33.1 (C-25), 19.7 (C-26), 20.0 (C-27), 17.6 (C-28)。以上数据与文献[7]报道的麦角甾-4, 6, 8 (14), 22-四烯-3-酮一致。

化合物 7 无色针状结晶(氯仿),用石油醚-丙酮(80∶20)、石油醚-醋酸乙酯(80∶20)、氯仿-甲醇(98∶2)薄层展开, Rf值与 β-谷甾醇标准品均一致,混合熔点不下降,鉴定该化合物为 β-谷甾醇。

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Chemical constituents from root of Actinidia chinensis

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[Abstract] **Objective:** To study the chemical constituents from the root of *Actinidia chinensis*. **Method:** The roots of *A. chinensis* were extracted with 95% EtOH. The EtOH extract was suspended in H_2O and extracted with petroleum ether, EtOAc and BuOH successively. The compounds were isolated with column chromatography from the EtOAc fraction, and elucidated on the basis of spectral analysis (MS, IR, ^{1}H-NMR, ^{13}C-NMR). **Result:** Seven compounds were isolated from the root of *A. chinensis*, and the structures were identified as 2α-hydroxyoleanolic acid (**1**), 2α-hydroxyursolic acid (**2**), euscaphic acid (**3**), 23-hydroxyursolic acid (**4**), 3β-O-acetylursolic acid (**5**), ergosta-4, 6, 8, (14), 22-tetraen-3-one (**6**), β-steriol (**7**). **Conclusion:** All the compounds were obtained from the root of *A. chinensis* for the first time.

[Key word] *Actinidia chinensis*; triterpenoids; sterides

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