

无梗五加果实中齐墩果酸苷的分离与鉴定

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[摘要] **目的:**研究无梗五加 *Acanthopanax sessiliflorus* (Ruqr. et Maxim) Seem. 果实的化学成分。**方法:**采用溶剂提取法、溶剂萃取法、硅胶柱色谱法、凝胶柱色谱法、重结晶法对无梗五加果实中的化合物进行分离纯化;根据光谱数据和理化性质确定化合物结构。**结果:**分离并鉴定了 6 个化合物,分别为齐墩果酸-3-*O*- β -*D*-葡萄糖酸甲酯苷(1),齐墩果酸-3-*O*- α -*L*-阿拉伯糖苷(2),齐墩果酸-3-*O*- β -*D*-葡萄糖酸正丁酯苷(3),齐墩果酸-3-*O*- β -*D*-葡萄糖醛酸苷(4),齐墩果酸(5),3-*O*-[(α -*L*-arabinopyranosyl)-(1 \rightarrow 2)]-[- β -*D*-glucuronopyranosyl-6-*O*-methyl ester]-olean-12-ene-28-olic acid(6)。**结论:**化合物 2,3 为首次从无梗五加果实中分离得到。

[关键词] 无梗五加;齐墩果酸苷;结构鉴定

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Isolation and Identification Glycosides of Oleanolic Acid from Fruits of *Acanthopanax sessiliflorus*

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[Abstract] **Objective:** To study the chemical constituents of the fruits of *Acanthopanax sessiliflorus*. **Method:** The methods of solvent extraction, silica gel column chromatography, Sephadex LH-20 column chromatography and recrystallization were used for the isolation; spectroscopy was used for the structure identification. **Result:** Six compounds were isolated and identified as oleanolic acid 3-*O*-6'-methyl- β -*D*-glucuronopyranoside (1), 3-*O*- α -*L*-arabinopyranosyl-oleanolic acid (2), oleanolic acid 3-*O*-6'-butyl- β -*D*-glucurono-pyranoside (3), momordin lb (4), oleanolic acid (5), 3-*O*-[(α -*L*-arabinopyranosyl)-(1 \rightarrow 2)]-[-*D*-glucuronopyranosyl-6-*O*-methyl ester]-olean-12-ene-28-olic acid (6). **Conclusion:** Compounds 2, 3 were first isolated from the fruits of *A. sessiliflorus*.

[Key words] *Acanthopanax sessiliflorus*; glycosides of oleanolic acid; structure identification

无梗五加又称短梗五加,为五加科五加属多年生药膳两用植物^[1]。在我国东北地区,无梗五加与刺五加经常混用,未见不良反应报道。为扩大药用资源,无梗五加现已引起国内外学者的广泛关注。

有报道无梗五加果具有抗肿瘤等作用,无梗五加果的饮料也已开发上市。本课题对无梗五加果的化学成分进行研究,分离得到 1 个齐墩果酸和 5 个齐墩果酸苷。

1 仪器与材料

Bruker-600 型核磁共振仪(瑞士 Bruker 公司), Sephadex LH-20 (瑞士 Pharmacia 公司),柱色谱硅胶(75~150,50~75 μ m,青岛海洋化工厂),薄层色谱(HF₂₅₄,青岛海洋化工厂),其他试剂均为分析纯。实验材料采自丹东市郊,经辽宁中医药大学植物教研室王冰教授鉴定为无梗五加 *Acanthopanax*

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sessiliflorus (Ruqr. et Maxim) Seem. 的果实。

2 提取与分离

取无梗五加果实 10 kg, 捣碎, 以 95% 乙醇回流提取 3 次, 每次 2 h, 滤过, 合并提取液, 回收乙醇, 得浓缩液。将浓缩液加 2 倍量的水稀释, 先后分别用与药液等体积的石油醚、乙酸乙酯以及正丁醇进行萃取, 各萃取 3 次。回收溶剂, 得到石油醚层 173.5 g, 乙酸乙酯层 166.0 g, 正丁醇层 601.9 g。其中对乙酸乙酯萃取物进行硅胶柱色谱分离, 氯仿-甲醇梯度洗脱(90:1~1:1), 每个流份收集 500 mL, TLC 检查合并相同组分, 共得到 12 份样品。Fr. 5 经硅胶柱色谱(氯仿-甲醇 10:1~2:1)和 Sephadex LH-20(氯仿-甲醇 1:1)得到化合物 1。Fr. 10 经硅胶柱色谱(氯仿-甲醇-水 10:1:1 d~1:1:1 d), 第 55 流份析出白色粉末, 以甲醇洗涤除去杂质, 得到化合物 2。取正丁醇萃取物进行硅胶柱色谱分离, 氯仿-甲醇梯度洗脱(体积比 90:1~1:1), 每个流份收集 500 mL, TLC 检识后合并相似流份得到 20 份样品。Fr. 2 经硅胶柱色谱(氯仿-甲醇 500:1~10:1)和 Sephadex LH-20(氯仿-甲醇 1:1)得到化合物 3。Fr. 3 经硅胶柱色谱(氯仿-甲醇 50:1~10:1), 第 131~136 流份合并, 经 Sephadex LH-20(氯仿-甲醇 1:1)得到化合物 4。第 140 流份再经硅胶柱色谱及 Sephadex LH-20(氯仿-甲醇 1:1), 得到化合物 5。Fr. 4 经硅胶柱色谱(氯仿-甲醇 10:1~2:1), 得白色结晶, 经甲醇重结晶, 得到化合物 6。

3 结构鉴定

化合物 1 白色粉末(甲醇)。¹H-NMR(Pyr, 600 MHz) δ : 0.82, 0.96, 1.05, 1.10, 1.22, 1.30, 1.42 (each 3H, s, tert-Me), 3.54 (3H, s, -OCH₃), 3.43 (2H, m, H-3, H-18), 5.40 (1H, br s, H-12); ¹³C-NMR(Pry, 150 MHz) δ : 180.2 (C-28), 144.8 (C-13), 124.1 (C-12), 89.1 (C-3), 55.8 (C-5), 52.0 (-OMe), 48.0 (C-9), 46.7 (C-17), 46.5 (C-19), 42.2 (C-14), 42.0 (C-18), 39.7 (C-8), 39.5 (C-4), 38.6 (C-1), 37.0 (C-10), 34.2 (C-29), 33.4 (C-21), 33.2 (C-7), 33.2 (C-22), 31.0 (C-20), 28.3 (C-15), 28.2 (C-23), 26.6 (C-2), 26.2 (C-27), 23.8 (C-30), 23.8 (C-16), 23.8 (C-11), 18.5 (C-6), 17.4 (C-26), 16.9 (C-24), 15.4 (C-25), 170.9 (C-6'), 107.3 (C-1'), 75.4 (C-2'), 77.9 (C-3'), 77.2 (C-5'), 73.2 (C-4')。以上数据与文献[2]报道基本一致, 故鉴定为齐墩果酸-3-O- β -D-葡萄糖醛甲酯苷。

化合物 2 白色粉末(甲醇)。¹H-NMR(Pyr, 600

MHz) δ : 0.82, 0.98, 1.01, 1.08, 1.20, 1.30, 1.44 (each 3H, s, tert-Me), 3.29 (2H, m, H-3, H-18), 5.47 (1H, br s, H-12); ¹³C-NMR(Pry, 150 MHz) δ : 180.2 (C-28), 144.9 (C-13), 123.2 (C-12), 89.1 (C-3), 55.9 (C-5), 49.7 (C-9), 48.0 (C-17), 46.7 (C-19), 42.2 (C-14), 42.0 (C-18), 39.8 (C-8), 39.6 (C-4), 38.7 (C-1), 37.0 (C-10), 34.3 (C-21), 33.3 (C-7), 33.3 (C-22), 31.0 (C-20), 28.4 (C-15), 28.0 (C-23), 26.3 (C-27), 23.8 (C-30), 23.8 (C-16), 23.8 (C-11), 18.5 (C-6), 17.4 (C-26), 16.5 (C-24), 15.5 (C-25), 106.8 (C-1'), 74.2 (C-2'), 73.8 (C-3'), 69.2 (C-4'), 67.1 (C-5')。以上数据与文献[3]报道基本一致, 故鉴定为齐墩果酸-3-O- α -L-阿拉伯糖苷。

化合物 3 白色粉末(甲醇)。¹H-NMR(Pyr, 600 MHz) δ : 0.89, 0.92, 0.96, 1.02, 1.06, 1.22, 1.30 (each 3H, s, tert-Me), 3.20 (2H, m, H-3, H-18), 5.66 (1H, br s, H-12); ¹³C-NMR(Pry, 150 MHz) δ : 180.2 (C-28), 144.9 (C-13), 122.5 (C-12), 89.1 (C-3), 55.8 (C-5), 48.0 (C-9), 46.7 (C-17), 46.5 (C-19), 42.2 (C-14), 42.0 (C-18), 39.7 (C-8), 39.5 (C-4), 38.6 (C-1), 37.0 (C-10), 34.2 (C-29), 33.3 (C-21), 33.3 (C-7), 33.2 (C-22), 31.0 (C-20), 28.3 (C-15), 28.1 (C-23), 26.6 (C-2), 26.2 (C-27), 23.8 (C-30), 23.8 (C-16), 23.8 (C-11), 18.5 (C-6), 17.4 (C-26), 17.0 (C-24), 15.5 (C-25), 170.4 (C-6'), 107.4 (C-1'), 75.5 (C-2'), 78.0 (C-3'), 77.4 (C-5'), 73.1 (C-4'), 64.9 (C-1''), 31.4 (C-2''), 19.3 (C-3''), 13.7 (C-4'')。以上数据与文献[4]报道基本一致, 故鉴定为齐墩果酸-3-O- β -D-葡萄糖醛正丁酯苷。

化合物 4 白色粉末(甲醇)。¹H-NMR(Pyr, 600 MHz) δ : 0.83, 0.91, 0.92, 1.01, 1.12, 1.24, 1.35 (each 3H, s, tert-Me), 3.52 (2H, m, H-3, H-18), 5.49 (1H, br s, H-12); ¹³C-NMR(CDCl₃, 150 MHz) δ : 180.2 (C-28), 144.8 (C-13), 122.5 (C-12), 89.0 (C-3), 55.8 (C-5), 48.0 (C-9), 46.7 (C-17), 46.5 (C-19), 42.2 (C-14), 42.0 (C-18), 39.7 (C-8), 39.5 (C-4), 38.6 (C-1), 37.0 (C-10), 34.2 (C-29), 33.3 (C-21), 33.3 (C-7), 33.2 (C-22), 31.0 (C-20), 28.3 (C-15), 28.2 (C-23), 26.6 (C-2), 26.2 (C-27), 23.6 (C-30), 23.8 (C-30), 23.8 (C-11), 23.7 (C-16), 18.5 (C-6), 17.4 (C-26), 17.0 (C-24), 15.4 (C-25), 172.9 (C-6'), 107.3 (C-1'), 75.6 (C-2'), 78.2 (C-3'), 77.9 (C-5'), 73.2 (C-4')。以上数据与文献[5]

报道基本一致,故鉴定为齐墩果酸-3-*O*- β -D 葡萄糖醛酸苷。

化合物 5 白色粉末(甲醇)。¹H-NMR(Pyr, 600 MHz) δ : 0.83, 0.92, 0.95, 1.03, 1.06, 1.26, 1.38 (each 3H, s, tert-Me), 3.58(2H, m, H-3, H-18), 5.40(1H, br s, H-12); ¹³C-NMR(Pyr, 150 MHz) δ : 183.6(C-28), 143.6(C-13), 122.6(C-12), 79.0(C-3), 55.2(C-5), 47.6(C-9), 46.5(C-17), 45.8(C-19), 41.5(C-14), 40.9(C-18), 39.2(C-8), 38.7(C-4), 38.4(C-1), 37.1(C-10), 33.8(C-21), 33.1(C-29), 32.6(C-7), 32.4(C-22), 30.6(C-20), 28.1(C-23), 27.6(C-15), 27.1(C-2), 25.9(C-27), 23.6(C-30), 23.4(C-16), 22.9(C-11), 18.3(C-6), 17.1(C-26), 15.5(C-24), 15.3(C-25)。以上数据与文献[6]报道基本一致,故鉴定为齐墩果酸。

化合物 6 白色粉末(甲醇)。¹H-NMR(Pyr, 600 MHz) δ : 0.81, 0.93, 0.96, 1.01, 1.04, 1.25, 1.36(each 3H, s, tert-Me), 3.58(2H, m, H-3, H-18), 5.40(1H, br s, H-12), 5.18(1H, d, $J = 6.6$, H-1''), 5.00(1H, d, $J = 7.5$, H-1'), 3.71(3H, s, -OCH₃); ¹³C-NMR(Pyr, 150 MHz) δ : 180.2(C-28), 144.8(C-13), 122.6(C-12), 89.3(C-3), 55.8(C-5), 48.0(C-9), 46.8(C-17), 46.5(C-19), 42.2(C-14), 42.0(C-18), 39.7(C-8), 39.6(C-4), 38.7(C-1), 37.0(C-10), 34.3(C-29), 33.3(C-21), 33.3(C-7), 33.2(C-22), 31.0(C-20), 28.3(C-15), 28.0(C-23), 26.7(C-2), 26.2(C-27), 23.8(C-16), 23.8(C-11), 18.5(C-6), 17.4(C-26), 16.4(C-24), 15.5(C-25); 170.9(C-6'), 107.3(C-1'), 75.6(C-2'), 78.2(C-

3'), 77.9(C-5'), 73.2(C-4'), 106.7(C-1''), 74.3(C-2''), 72.9(C-3''), 69.2(C-5''), 67.1(C-4''); 52.1(-OCH₃)。以上数据与文献[7]报道基本一致,因此鉴定为 3-*O*-[(α -L-arabinopyranosyl)-(1 \rightarrow 2)]-[β -D-glucuronopyranosyl-6-*O*-methylester]-olean-12-ene-28-olic acid。

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