

鼠曲草乙酸乙酯部位化学成分 II

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[摘要] 目的: 研究鼠曲草乙酸乙酯部位化学成分。方法: 采用硅胶柱色谱、Sephadex LH-20 等分离纯化手段相结合对鼠曲草进行分离纯化。通过理化性质和波谱数据(¹H-NMR, ¹³C-NMR)进行结构鉴定。结果: 从鼠曲草中分离鉴定了13个化合物, 分别鉴定为咖啡酸乙酯(1), 原儿茶酸乙酯(2), 对羟基肉桂酸(3), 4-羟基苯乙酮(4), 原儿茶酸(5), 3-(4'-formylphenoxy)-4-methoxybenzaldehyde(6), desmethylyangonine-4'-glucopyranoside(7), 4'-hydroxydehydrokawain(8), 绿原酸(9), 1,4,5-三咖啡酰奎宁酸(10), 1,5-二咖啡酰奎宁酸(11), 1,5-二咖啡酰奎宁酸甲酯(12), 1,3-二咖啡酰奎宁酸(13)。结论: 化合物1, 2, 4~7, 10为首次从鼠曲草属植物中分离得到, 化合物3, 8为首次从菊科植物中分离得到。

[关键词] 鼠曲草; 化学成分; 鼠曲草属; 结构鉴定

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Chemical Constituents of Ethyl Acetate Extract Part of *Gnaphalium affine* II

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[Abstract] **Objective:** This article aimed to study chemical constituents of *Gnaphalium affine*. **Method:**

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Compounds were obtained from the ethyl acetate extraction of *G. affine* by silica gel column chromatography and Sephadex LH-20. Their structures were elucidated according to spectral data and physiochemical properties.

Result: Thirteen compounds were isolated from *G. affine* and identified as ethyl caffeate (**1**), protocatechuic acid (**2**), *E*- β -hydroxy-cinnamic acid (**3**), 4-hydroxyacetophen-one (**4**), protocatechuic acid ethyl ester (**5**), 3-(4'-formylphenoxy)-4-methoxybenzaldehyde (**6**), desmethylyangonine-4'-glucopyranoside (**7**), 4'-hydroxydehydrokawain (**8**), chlorogenic acid (**9**), 1, 4, 5-tri-*O*-caffeoylquinic acid (**10**), 1, 5-di-*O*-caffeoylquinic acid (**11**), 1, 5-di-*O*-caffeoylquinic acid methyl ester (**12**), and 1, 3-di-*O*-caffeoylquinic acid (**13**). **Conclusion:** Compounds **1**, **2**, **4-7** and **10** were isolated from *Gnaphalium* for the first time, and compounds **3** and **8** were isolated from Compositae for the first time.

[**Key words**] *Gnaphalium affine*; chemical constituent; *Gnaphalium*; structural identification

鼠曲草又名鼠耳草、清明菜、追骨风。该属植物在全世界约 200 种,我国有 19 种,南北均产,主要分布于长江流域和珠江流域。本草味甘,微酸,性平,归肺经,具有止咳化痰、平喘、祛风湿等功效,用于治疗风湿痹痛。清明期间,福建、江西、浙江等民间常采用鼠曲草做鼠曲饼或清明果,是值得开发药食同源的植物资源。据文献报道鼠曲草主要含黄酮及其苷类^[1-3],挥发油^[4-6]和萜类^[7],还含有氨基酸^[8]。为进一步研究鼠曲草的化学成分,笔者对鼠曲草的乙酸乙酯萃取部位进行了分离,结果鉴定了 13 个化合物,其中化合物 **1, 2, 4 ~ 7, 10** 为首次从鼠曲草属植物中分到,化合物 **3, 8** 为首次从菊科植物中分离得到,化合物均首次从鼠曲草中分离得到。

1 材料

MAT-212 型质谱仪(美国 Varian 公司), AC-600P 型核磁共振仪(德国 Bruker 公司), Yanaco 显微熔点测定仪(日本 Yanaco 公司), CPA225D 型电光分析天平(德国 Sartorius 公司), ZF-20D 型暗箱式紫外分析仪(上海顾村电光仪器厂), 柱层析硅胶、薄层硅胶(山东烟台江友硅胶开发有限公司)。碘蒸气, 10% 硫酸乙醇溶液(国药集团有限公司); 其余试剂均为市售分析纯。

鼠曲草药材于 2008 年 9 月购自安徽亳州药材市场,经第二军医大学生药教研室张汉明教授鉴定为菊科鼠曲草属植物鼠曲草 *Gnaphalium affine* D. Don 的干燥全草,标本(sln-sqc-20080928)存放于第二军医大学药学院生药教研室。

2 提取分离

鼠曲草干燥全草 27.0 kg 粉碎,80% 乙醇回流提取 3 次,合并提取液回收乙醇,浓缩至干得浸膏 3 370 g。浸膏用水混悬,依次用石油醚、乙酸乙酯、正丁醇萃取,浓缩回收萃取溶剂得到 4 个极性部位,其中石油醚部位 450 g,乙酸乙酯部位 550 g,正丁醇

部位 380 g。取乙酸乙酯部位萃取物 400 g 用硅胶柱色谱(100 ~ 200 目) 4 kg,以二氯甲烷-甲醇(50:1 ~ 0:1)梯度洗脱。经薄层鉴别,合并相同流分得 Fr₁ ~ Fr₆ 共 6 部分。Fr₄ 经硅胶柱色谱(二氯甲烷-甲醇 30:1 ~ 0:1)梯度洗脱,得 Fr_{4.1} ~ Fr_{4.3} 部分。Fr_{4.1} 经 MCI 色谱柱(甲醇-水 3:7 ~ 1:0), Sephadex LH-20(二氯甲烷-甲醇 1:1)反复洗脱纯化,得到化合物 **1**(5 mg), **2**(9 mg), **3**(8 mg); Fr_{4.2} 经 Sephadex LH-20 色谱柱(甲醇-水 4:6 ~ 1:0)洗脱,经 Sephadex LH-20(甲醇)反复纯化,得化合物 **4**(5 mg) 和 **5**(9 mg), Fr_{4.3} 经 Sephadex LH-20(甲醇-水 8:2) 和 ODS 反相色谱柱(甲醇-水 3:7 ~ 6:4) 得化合物 **11**(340 mg); Fr₅ 经色谱柱 MCI(甲醇-水 0:1 ~ 1:0), 梯度洗脱得 Fr_{5.1} ~ Fr_{5.3}。Fr_{5.1} 经 Sephadex LH-20(甲醇-水 8:2 ~ 1:0)洗脱,得化合物 **6**(15 mg), Fr_{5.2} 经 Sephadex LH-20(甲醇-水 8:2) 得化合物 **7**(10 mg); Fr_{5.3} 经 ODS 反相色谱(甲醇-水 4:6 ~ 8:2) 得化合物 **9**(18 mg); Fr₆ 经 ODS 反相(甲醇-水 2:8 ~ 1:0), 梯度洗脱得 Fr_{6.1}, Fr_{6.2} 两部分。Fr_{6.1} 经 ODS 反相(甲醇-水 3:7 ~ 8:2), 得化合物 **10**(35 mg), **12**(450 mg), Fr_{6.2} 经 ODS 反相(甲醇-水 4:6 ~ 1:0), Sephadex LH-20(甲醇-水 8:2 ~ 1:0) 得化合物 **8**(23 mg) 和 **13**(125 mg)。

3 结构鉴定

化合物 **1** 淡黄色针晶(乙酸乙酯), 162 ~ 165 °C, ESI-MS *m/z* 207 [M - H]⁻。¹H-NMR (600 MHz, CDCl₃) δ : 7.60 (1H, d, *J* = 15.6 Hz, H-7), 7.12 (1H, d, *J* = 1.8 Hz, H-2), 7.03 (1H, dd, *J* = 1.8, 7.8 Hz, H-6), 6.90 (1H, d, *J* = 7.8 Hz, H-5), 6.28 (1H, d, *J* = 15.6 Hz, H-8), 5.86 (1H, brs, 4-OH), 5.72 (1H, brs, 3-OH), 4.28 (2H, q, *J* = 7.2 Hz, -CH₂-), 1.35 (1H, t, *J* = 7.2 Hz, -CH₃)。 ¹³C-NMR (150 MHz, CDCl₃) δ : 166.5 (C-9), 127.6

(C-1), 146.1 (C-4), 144.7 (C-3), 143.7 (C-7), 122.4 (C-6), 115.6 (C-5), 115.5 (C-8), 114.3 (C-2), 60.6 ($-\text{CH}_2^-$), 14.3 ($-\text{CH}_3$)。以上数据与文献报道[9]的基本一致,因此确定化合物**1**为咖啡酸乙酯。

化合物**2** 无色针状结晶,195~198℃,ESI-MS m/z 155 $[\text{M} + \text{H}]^+$ 。¹H-NMR (600 MHz, DMSO- d_6) δ : 7.34 (1H, d, $J = 1.8$ Hz, H-2), 7.30 (1H, dd, $J = 1.8, 7.8$ Hz, H-6), 6.78 (1H, d, $J = 7.8$ Hz, H-5); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 121.7 (C-1), 116.6 (C-2), 144.9 (C-3), 150.0 (C-4), 115.2 (C-5), 121.9 (C-6), 167.4 (C-7)。以上数据与文献报道[10]的基本一致,因此确定化合物**2**为原儿茶酸。

化合物**3** 白色结晶,210~215℃,ESI-MS m/z 163 $[\text{M} - \text{H}]^-$ 。¹H-NMR (600 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 8.08 (1H, d, $J = 15.6$ Hz, H-7), 7.61 (2H, d, $J = 8.4$ Hz, H-2, 6), 7.14 (2H, d, $J = 8.4$ Hz, H-3, 5), 6.81 (1H, d, $J = 15.6$ Hz, H-8); ¹³C-NMR (150 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 126.3 (C-1), 130.4 (C-2, 6), 116.7 (C-3, 5), 161.0 (C-4), 144.5 (C-7), 116.9 (C-8), 169.6 (C-9)。以上数据与文献[10]基本一致,因此确定化合物**3**为对羟基反式肉桂酸。

化合物**4** 白色针晶,110~112℃,ESI-MS m/z 137 $[\text{M} + \text{H}]^+$ 。¹H-NMR (600 MHz, CD_3OD) δ : 7.88 (2H, d, $J = 8.4$ Hz, H-2, 6), 6.84 (2H, d, $J = 8.4$ Hz, H-3, 5), 2.52 (3H, s, $-\text{CH}_3$); ¹³C-NMR (150 MHz, CD_3OD) δ : 199.3 (C-7), 163.7 (C-4), 131.9 (C-2, 6), 129.9 (C-1), 116.0 (C-3, 5), 26.1 (C-8)。以上数据与文献[11]基本一致,故鉴定为4-羟基苯乙酮。

化合物**5** 无色针晶(乙酸乙酯),133~136℃,ESI-MS m/z 183 $[\text{M} + \text{H}]^+$ 。¹H-NMR (600 MHz, CD_3OD) δ : 7.42 (1H, d, $J = 1.8$ Hz, H-2), 7.41 (1H, dd, $J = 1.8, 8.4$ Hz, H-6), 6.80 (1H, d, $J = 8.4$ Hz, H-5), 4.28 (2H, q, $J = 7.2$ Hz, $-\text{CH}_2^-$), 1.35 (1H, t, $J = 7.2$ Hz, $-\text{CH}_3$); ¹³C-NMR (150 MHz, CD_3OD) δ : 168.4 (C-7), 151.7 (C-4), 146.2 (C-3), 123.6 (C-6), 122.9 (C-1), 117.4 (C-5), 115.9 (C-2), 61.7 ($-\text{CH}_2^-$), 14.7 ($-\text{CH}_3$)。以上数据与化合物**2**基本一致,不同的是成酯了,因此确定化合物**5**为原儿茶酸乙酯。化合物**5**加入药材中,HPLC分析,化合物**5**的含量明显增高,证实化合物**5**存在于药材中。

化合物**6** 无色粉末,116~119℃,ESI-MS m/z 257 $[\text{M} + \text{H}]^+$ 。¹H-NMR (600 MHz, CD_3OD) δ : 9.76 (1H, s, $-\text{CHO}$), 9.74 (1H, s, $-\text{CHO}$), 7.8 (2H, d, $J = 8.4$ Hz, H-3', 5'), 7.43 (1H, d, $J = 1.8$ Hz, H-2), 7.42 (1H, dd, $J = 1.8, 8.4$ Hz, H-6), 6.91 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.94 (1H, d, $J = 8.4$ Hz, H-5), 3.92 (3H, s, $-\text{OCH}_3$); ¹³C-NMR (150 MHz, CD_3OD) δ : 164.8 (C-1'), 153.3 (C-4), 148.2 (C-3), 132.0 (C-3', 5'), 129.2 (C-1), 128.8 (C-4'), 126.5 (C-6), 115.4 (C-2', 6'), 114.9 (C-5), 109.0 (C-2), 54.9 ($-\text{OCH}_3$)。以上数据与文献[12]报道的基本一致,因此确定化合物**6**为3-(4'-formylphenoxy)-4-methoxybenzaldehyde。

化合物**7** 黄色粉末,184~187℃,ESI-MS m/z 811 $[2\text{M} - \text{H}]^-$, 835 $[2\text{M} + \text{Na}]^+$ 。¹H-NMR (600 MHz, DMSO- d_6) δ : 7.60 (2H, d, $J = 9.0$ Hz, H-2', 6'), 7.28 (1H, d, $J = 16.2$ Hz, H-8), 7.05 (2H, d, $J = 9.0$ Hz, H-3', 5'), 6.87 (1H, d, $J = 16.2$ Hz, H-7), 6.26 (1H, d, $J = 1.8$ Hz, H-5), 5.61 (1H, d, $J = 1.8$ Hz, H-3), 4.92 (1H, d, $J = 7.8$ Hz, H-1''), 3.95 (1H, m, H-5''), 3.83 (3H, s, $-\text{OCH}_3$), 3.71 (1H, m, H-3''), 3.47 (1H, m, H-6a), 3.35 (1H, m, H-6b), 3.28 (1H, m, H-4''), 3.16 (1H, m, H-2''); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 170.7 (C-4), 162.6 (C-6), 158.2 (C-5), 158.2 (C-4'), 133.7 (C-8), 128.8 (C-2', 6'), 128.7 (C-1'), 117.6 (C-7), 116.4 (C-3', 5'), 100.6 (C-1''), 99.9 (C-5), 88.3 (C-3), 76.9 (C-3''), 76.4 (C-3''), 73.1 (C-2''), 69.6 (C-4''), 60.5 (C-6''), 56.3 ($-\text{OCH}_3$)。以上数据与文献[13]基本一致,故鉴定化合物**7**为desmethylyangonine-4'-glucopyranoside。

化合物**8** 黄色粉末,145~147℃,ESI-MS m/z 245 $[\text{M} + \text{H}]^+$ 。¹H-NMR和¹³C-NMR数据和化合物**7**相似,只相差1个葡萄糖,¹H-NMR (600 MHz, DMSO- d_6) δ : 7.49 (2H, d, $J = 8.4$ Hz, H-2', 6'), 7.25 (1H, d, $J = 16.2$ Hz, H-8), 6.80 (2H, d, $J = 8.4$ Hz, H-3', 5'), 6.78 (1H, dd, $J = 16.2, 1.8$ Hz, H-7), 6.22 (1H, d, $J = 1.8$ Hz, H-5), 5.59 (1H, d, $J = 1.8$ Hz, H-3), 3.82 (3H, s, $4-\text{OCH}_3$); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 162.7 (C-2), 88.0 (C-3), 170.9 (C-4), 56.3 ($4-\text{OCH}_3$), 100.0 (C-5), 158.9 (C-6), 116.1 (C-7), 134.3 (C-8), 126.2 (C-1'), 129.2 (C-2', 6'), 115.7 (H-3', 5'), 158.9 (C-4')。以上数据与文献[14]基本一

致,确定化合物 **8** 为 4'-hydroxydehydrokawain。

化合物 **9** 淡黄色无定型粉末, 205 ~ 208 °C, ESI-MS m/z 353 [M - H]⁻。¹H-NMR (600 MHz, DMSO- d_6) δ : 7.44 (1H, d, J = 15.6 Hz, H-7'), 7.05 (1H, d, J = 1.8 Hz, H-2'), 6.97 (1H, dd, J = 2.4, 8.4 Hz, H-6'), 6.77 (1H, d, J = 8.4 Hz, H-5'), 6.17 (1H, d, J = 16.2 Hz, H-8'), 5.08 (1H, m, H-3), 3.95 (1H, m, H-4), 3.57 (1H, m, H-5), 2.02 (1H, m, H-2 β), 1.96 (2H, m, H-6), 1.78 (1H, m, H-2 α); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 175.2 (COOH), 165.9 (C-9'), 148.4 (C-4'), 145.5 (C-3'), 145.1 (C-7'), 125.7 (C-1'), 121.5 (C-6'), 115.9 (C-2'), 114.8 (C-5'), 114.4 (C-8'), 73.7 (C-1), 70.9 (C-3), 70.6 (C-4), 68.4 (C-5), 36.5 (C-2, 6)。以上数据与文献[15]基本一致,因此确定化合物 **9** 为绿原酸。

化合物 **10** 黄色无定型粉末, 223 ~ 227 °C, HR-ESI-MS m/z 679.135 [M + H]⁺。¹H-NMR (600 MHz, DMSO- d_6) δ : 7.08 (1H, d, J = 1.8 Hz, H-2'), 7.06 (1H, d, J = 1.8 Hz, H-2''), 7.03 (1H, d, J = 1.8 Hz, H-2'''), 7.02 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 6.92 (1H, dd, J = 8.4, 1.8 Hz, H-6''); 6.87 (1H, J = 1.8, 8.4 Hz, H-6''), 6.81 (1H, d, J = 8.4 Hz, H-5'), 6.75 (2H, d J = 8.4 Hz, H-5'', 5'''), 7.51 (1H, d, J = 15.6 Hz, H-7'), 6.25 (1H, d, J = 15.6 Hz, H-8'), 7.49 (1H, d, J = 15.6 Hz, H-7''), 6.21 (1H, d, J = 15.6 Hz, H-8''), 7.41 (1H, d, J = 15.6 Hz, H-7'''), 6.11 (1H, d, J = 15.6 Hz, H-8'''); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 173.9 (C-7), 165.9 (C-9'), 165.8 (C-9''), 165.3 (C-9'''), 148.5 (C-4'), 148.3 (C-4''), 148.1 (C-4'''), 145.8 (C-3'), 145.6 (C-7''), 145.5 (C-7''', 3'', 3'''), 145.3 (C-7'), 125.4 (C-1'), 125.2 (C-1''), 125.1 (C-1'''), 121.4 (C-6'), 121.3 (C-6'', 6'''), 115.9 (C-5'), 115.8 (C-5'', C-5'''), 114.8 (C-2', 2''), 114.6 (C-2'''), 114.6 (C-8'), 114.3 (C-8''), 113.9 (C-8'''), 80.9 (C-1), 75.0 (C-4), 67.1 (C-5), 66.3 (C-3), 37.8 (C-6), 34.7 (C-2)。以上数据与文献[16]基本一致,故鉴定为 1,4,5-三咖啡酰奎宁酸。

化合物 **11** 淡黄色粉末, 226 ~ 229 °C, ESI-MS m/z 517 [M + H]⁺, 三氯化铁-铁氰化钾反应阳性, 溴甲酚绿反应阳性。¹H-NMR (600 MHz, DMSO- d_6) δ : 7.47 (1H, d, J = 15.6 Hz, H-7'), 7.41 (1H, d, J = 15.6 Hz, H-7''), 7.08 (1H, d, J = 1.8 Hz, H-

2'), 7.03 (1H, d, J = 1.8 Hz, H-2''), 7.00 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 6.92 (1H, dd, J = 8.4, 1.8 Hz, H-6''), 6.76 (1H, d, J = 8.4 Hz, H-5'), 6.74 (1H, d, J = 8.4 Hz, H-5''), 6.24 (1H, d, J = 15.6 Hz, H-8'), 6.17 (1H, d, J = 15.6 Hz, H-8''), 5.22 (1H, m, H-5), 4.08 (1H, m, H-3), 3.61 (1H, dd, J = 5.4, 8.4 Hz, H-4), 2.53 (1H, dd, J = 12.0, 7.2 Hz, H-2a), 2.34 (1H, dd, J = 4.8, 12.0 Hz, H-6a), 2.20 (1H, dd, J = 12.0, 6.0 Hz, H-2b), 1.81 (1H, dd, J = 4.8, 7.2 Hz H-6b); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 174.4 (C-7), 166.3 (C-9'), 165.0 (C-9''), 149.0 (C-4'), 148.2 (C-4''), 145.9 (C-3', 3''), 144.8 (C-7'), 144.6 (C-7''), 125.6 (C-1'), 125.5 (C-1''), 121.2 (C-6'), 120.3 (C-6''), 116.0 (C-5'), 115.9 (C-5''), 114.9 (C-2', 2''), 114.2 (C-8', 8''), 81.9 (C-1), 72.4 (C-4), 70.4 (C-5), 68.9 (C-3), 37.6 (C-6), 34.9 (C-2)。以上数据与文献[17]基本一致,该化合物鉴定为 1,5-二咖啡酰奎宁酸(1,5-di-*O*-caffeoyl quinic acid)。

化合物 **12** 淡黄色无定型粉末, 229 ~ 231 °C, ESI-MS m/z 531 [M + H]⁺, 三氯化铁-铁氰化钾反应阳性, 溴甲酚绿反应阳性。¹H-NMR (600 MHz, DMSO- d_6) δ : 7.47 (1H, d, J = 15.6 Hz, H-7'), 7.41 (1H, d, J = 15.6 Hz, H-7''), 7.08 (1H, d, J = 1.8 Hz, H-2'), 7.03 (1H, d, J = 1.8 Hz, H-2''), 7.00 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 6.92 (1H, dd, J = 8.4, 1.8 Hz, H-6''), 6.76 (1H, d, J = 8.4 Hz, H-5'), 6.74 (1H, d, J = 8.4 Hz, H-5''), 6.24 (1H, d, J = 15.6 Hz, H-8'), 6.17 (1H, d, J = 15.6 Hz, H-8''), 5.22 (1H, m, H-5), 4.08 (1H, m, H-3), 3.61 (1H, dd, J = 6.0, 8.4 Hz, H-4), 3.17 (3H, s, -OCH₃), 2.52 (1H, dd, J = 12.0, 7.2 Hz, H-2a), 2.34 (1H, dd, J = 4.8, 12.0 Hz, H-6a), 2.20 (1H, dd, J = 12.0, 6.0 Hz, H-2b), 1.81 (1H, dd, H-6_b); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 125.6 (C-1'), 125.5 (C-1''), 114.9 (C-2'), 114.9 (C-2''), 145.9 (C-3', 3''), 149.0 (C-4'), 148.2 (C-4''), 116.0 (C-5'), 115.9 (C-5''), 121.2 (C-6'), 120.3 (C-6''), 144.8 (C-7'), 144.6 (C-7''), 114.2 (C-8', 8''), 166.3 (C-9'), 165.0 (C-9''), 67.3 (-OCH₃)。发现该化合物与化合物 **11** 基本相同,不同的是多了一个 -OCH₃。故鉴定化合物 **12** 的结构为 1,5-二咖啡酰奎宁酸甲酯。

化合物 **13** 淡黄色结晶, 225 ~ 227 °C, ESI-MS

m/z 517 [M + H]⁺, 三氯化铁-铁氰化钾反应阳性。¹H-NMR (600 MHz, DMSO-*d*₆) δ: 7.43 (1H, d, J = 15.6 Hz, H-7'), 7.45 (1H, d, J = 15.6 Hz, H-7''), 7.02 (1H, d, J = 1.8 Hz, H-2''), 6.98 (1H, d, J = 1.8 Hz, H-2'), 6.86 (1H, dd, J = 8.4, 1.8 Hz, H-6''), 6.68 (1H, d, J = 8.4 Hz, H-5''), 6.63 (1H, d, J = 8.4 Hz, H-5'), 6.18 (1H, d, J = 15.6 Hz, H-8''), 6.14 (1H, d, J = 15.6 Hz, H-8'), 5.20 (1H, t, J = 4.2 Hz, H-3), 4.18 (1H, ddd, J = 13.2, 9.0, 3.0 Hz, H-5), 3.59 (1H, dd, J = 12.96, 3.6 Hz, H-4), 2.43 (1H, dd, J = 15.6, 3.6 Hz, H-2a), 2.13 (2H, d, J = 12.0 Hz, H-6a), 2.08 (1H, d, J = 12.0 Hz, H-2b), 1.81 (1H, dd, J = 13.2, 12.0 Hz, H-6b); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ: 81.9 (C-1), 33.6 (C-2), 72.9 (C-3), 74.9 (C-4), 68.4 (C-5), 41.6 (C-6), 174.3 (C-7), 126.1 (C-1'), 125.8 (C-1''), 116.0 (C-2'), 115.6 (C-2''), 145.9 (C-3', 3''), 149.1 (C-4', C-4''), 116.4 (C-5'), 116.3 (C-5''), 121.2 (C-6'), 120.3 (C-6''), 148.9 (C-7'), 146.4 (C-7''), 115.5 (C-8'), 114.9 (C-8''), 166.3 (C-9'), 165.0 (C-9'')。与文献[18]基本一致, 故鉴定为 1, 3-二咖啡酰奎宁酸。

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