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# 锥序蜜心果中酚性成分的研究

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摘　要: 从锥序蜜心果的乙酸乙酯部分中分离到 5个化合物, 通过波谱数据或与已知化合物对照, 它们分别鉴定为(*E*)-3-(3-hydroxy-4-methoxyphenyl) acrylic acid carboxymethyl ester (**1**), 3, 4-二羟基苯甲酸 (**2**), 槲皮素-3-O-β-葡萄糖甙 (**3**), 山萘酚-3-O-α-鼠李糖甙(**4**) 和槲皮素-3-O-α-鼠李糖甙 (**5**), 以上化合物均为首次从该属植物中分离到。

关键词: 锥序蜜心果; 酚性成分

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# The Phenolic Components from *Saurauia napaulensis*

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**Abstract** Five compounds were isolated from ethyl acetate soluble fraction of *Saurauia napaulensis*. Their structures were elucidated as (*E*)-3-(3-hydroxy-4-methoxyphenyl) acrylic acid carboxymethyl ester (**1**), 3, 4-dihydroxybenzoic acid (**2**), quercetin-3-O-β-glucopyrannoside (**3**), kaempferol-3-O-α-rhamnoside (**4**) and quercetin 3-O-α-rhamnoside (**5**) by spectral methods. The structures of compounds **1-5** were elucidated on the basis of spectral evidence.

**Key words** *Saurauia napaulensis*; phenolic components

## Introduction

*Saurauia napaulensis*, an endemic species belonging to the family of Saurauiaceae, is distributed in Xishuangbanna of Yunnan Province. Some species of *Saurauia* were used in Chinese folk medicine for the treatment of fracture, injuries for falls, cold, cough, etc. Its unique taxonomic position attracted us to investigate the chemical constituent. In order to search for the active constituents from this plant, we recently investigated it and got five compounds from it, on the basis of spectral evidence, we identified them as (*E*)-3-(3-hydroxy-4-methoxyphenyl) acrylic acid carboxymethyl ester (**1**)[1], 3, 4-dihydroxybenzoic acid (**2**)[2], quercetin-3-O-β-glucopyrannoside (**3**)[3], kaempferol-3-O-α-rhamnoside (**4**)[4], quercetin 3-O-α-rhamnoside (**5**)[5]. All compounds were firstly isolated from this plant.

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## Experimental

### General experimental procedures

Melting points were determined on an XRC-1 micro-melting point apparatus (uncorrected). UV spectra were obtained from an UV 210A spectrometer. IR spectra were recorded with a Bio-Rad FTS-35 spectrometer. MS spectra were measured with a VG Auto Spec-3000 spectrometer; NMR experiments were conducted with Bruker AM-400 and a DRX-500 MHz instruments.

### Plant materials

The dried rhizomes of *Saurauia napaulensis* were collected in September 2005 from Xishuangbanna, Yunnan Province and identified by Prof. Zhang shuncheng. A voucher specimen was deposited in the laboratory of Phytochemistry at Kunming Institute of Botany, the Chinese Academy of Sciences.

### Extraction and isolation

The air-dried and powdered aerial parts (5.0 kg) were extracted 3 times with 70% MeOH under reflux (3 × 30 L) for 4, 3, 3 h, respectively. After concentrating of

the combined extracts, the residue was suspended in water and then extracted with petroleum ether, AcOEt and BuOH. The AcOEt soluble part (108 g) was subjected to column chromatography (CC) over silica gel eluting with chloroform/methanol (1∶0-0∶1) to give fractions Ⅰ-Ⅵ. Fraction Ⅲ (18 g) and Ⅴ (20 g), using MCI to remove chlorophyll of fraction Ⅲ (A-C), fraction B (2707 mg) was subjected to CC on silica gel eluting with chloroform/acetone (1∶0-0∶1), and then repeatedly subjected to Sephadex LH-20 and reversed-phase silica gel (RP-18) eluted with $H_2O$/MeOH (2∶8-0∶1), to give compound **1** (42 mg), **2** (26 mg), using MCI to remove chlorophyll of fraction Ⅴ (D-G), fraction E (6620 mg) was subjected to CC on silica gel eluted with chloroform/methanol (1∶0-5∶5) to give fraction E1-E6. E3 (516 mg) repeatedly subjected to Sephadex LH-20, reversed phase silica gel eluted with $H_2O$/MeOH (2∶8-9∶1), to give compounds **3** (37 mg), **4** (21 mg), **5** (17 mg).

**Identification**

**(*E*)-3-(3-Hydroxy-4-methoxyphenyl) acrylic acid carboxymethyl ester (1)** White needle (MeOH), mp. 170-171 ℃, $C_{12}H_{12}O_6$, IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3424, 1727, 1604, 1507, 1270, 671; UV $\lambda_{max}^{MeOH}$ nm: 324.60, 295.40, 242.80, 217.60; $^1$H NMR (400 MHz, $CD_3OD$) δ 7.08 (d, *J* = 2.0 Hz, H-2), 6.92 (d, *J* = 8.3 Hz, H-5), 7.04 (dd, *J* = 2.0, 8.3 Hz, H-6), 6.37 (d, *J* = 15.9, H-2′), 7.62 (d, *J* = 15.9 Hz, H-3′), 4.69 (s, H-2″), 3.86 (s, OMe); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 128.76 (s, C-1), 114.81 (d, C-2), 148.06 (s, C-3), 151.60 (s, C-4), 112.47 (d, C-5), 122.88 (d, C-6), 168.27 (s, C-1′), 115.50 (d, C-2′), 147.18 (d, C-3′), 172.52 (s, C-1″), 62.14 (t, C-2″), 56.23 (q, OMe).

**3, 4-Dihydroxybenzoic acid (2)** White needle (MeOH), mp. 204.5-205 ℃, $C_7H_6O_4$, IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3400, 3080, 2500, 1520, 1450, 761; negative FAB-MS *m/z* (%): 153 (100), 136 (1), 108 (2); $^1$H NMR (400 MHz, $CD_3OD$) δ 6.29 (1H, d, *J* = 8.4 Hz, H-5), 7.43 (1H, d, *J* = 2.0, 8.4 Hz, H-6), 7.41 (1H, d, *J* = 2.0 Hz, H-2); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 123.11 (s, C-1), 115.70 (d, C-2), 146.01 (s, C-3), 151.50 (s, C-4), 117.70 (d, C-5), 123.80 (d, C-6), 170.29 (s, C-7).

**Quercetin-3-O-β-glucopyranoside (3)** Yellow powder (MeOH), mp. 196-198 ℃, $C_{21}H_{20}O_{12}$, IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3418, 1655, 1606, 1518, 1203, 1084; UV $\lambda_{max}^{MeOH}$ nm: 273, 304, 375; negative FAB-MS *m/z* (%): 463 (47), 342 (11), 282 (7), 188 (19); $^1$H NMR (400 MHz, $C_5D_5N$) δ 6.24 (d, *J* = 1.9 Hz, H-6), 6.40 (d, *J* = 1.7 Hz, H-8), 6.90 (d, *J* = 8.5 Hz, H-5′), 7.62 (dd, *J* = 2.0, 8.5 Hz, H-6′), 7.90 (d, *J* = 2.0 Hz, H-2′), 5.27 (d, *J* = 7.5 Hz, H-1″); $^{13}$C NMR (125 MHz, $C_5D_5N$) δ 158.38 (s, C-2), 135.77 (s, C-3), 179.46 (s, C-4), 163.00 (s, C-5), 94.76 (d, C-6), 150.05 (s, C-7), 99.97 (d, C-8), 158.68 (s, C-9), 105.61 (s, C-10), 122.87 (s, C-1′), 116.16 (d, C-2′), 145.90 (s, C-3′), 149.91 (s, C-4′), 117.82 (d, C-5′), 122.97 (d, C-6′), 105.44 (d, C-1″), 73.23 (d, C-2″), 77.28 (d, C-3″), 70.03 (d, C-4″), 75.17 (d, C-5″), 61.99 (t, C-6″).

**Kaempferol-3-O-α-rhamnopynoside (4)** Yellow powder (MeOH), mp. 178-180 ℃, $C_{21}H_{20}O_{10}$, IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3200-3600, 1660; UV $\lambda_{max}^{MeOH}$ nm: 264, 313 sh, 363; negative FAB-MS *m/z* (%): 431 (45), 325 (100), 311 (65), 285 (26); $^1$H NMR (400 MHz, $CD_3OD$) δ 6.20 (d, *J* = 2.0 Hz, H-6), 6.38 (d, *J* = 2.0 Hz, H-8), 7.76 (d, *J* = 8.3 Hz, H-2′, H-6′), 6.93 (d, *J* = 8.3 Hz, H-3′, H-5′), 5.37 (d, *J* = 1.4 Hz, H-1″), 0.91 (d, *J* = 6.5 Hz, H-6″); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 158.59 (s, C-2), 136.25 (s, C-3), 179.67 (s, C-4), 163.25 (s, C-5), 94.77 (d, C-6), 165.88 (s, C-7), 99.90 (d, C-8), 159.32 (s, C-9), 105.98 (s, C-10), 122.67 (s, C-1″), 131.89 (d, C-2′, C-6′), 116.55 (d, C-3′, C-5′), 161.59 (s, C-4′), 103.52 (d, C-1″), 72.19 (d, C-2″), 72.03 (d, C-3″), 73.23 (d, C-4″), 71.94 (d, C-5″), 17.65 (q, C-6″).

**quercetin 3-O-α-rhamnopynoside (5)** $C_{21}H_{20}O_{11}$, yellow powder (MeOH), mp. 165-168 ℃, IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3200-3500, 1640, 1610; UV $\lambda_{max}^{MeOH}$ nm: 255, 265 sh, 301 sh, 350; negative FAB-MS *m/z* (%): 447 (100), 325 (8), 301 (43), 255 (16), 137 (18); $^1$H NMR (500 MHz, $CD_3OD$) δ 6.20 (s, H-6), 6.38 (s, H-8), 7.34 (d, *J* = 1.9 Hz, H-2′), 6.90 (d, *J* = 8.3 Hz, H-5′), 7.32 (dd, *J* = 8.3, 1.9 Hz, H-6′), 5.36 (br s,

H-1″), 0.94 (d, $J$ = 6.1 Hz, H-6″); $^{13}$C NMR (125 MHz, $CD_3OD$) δ: 157.1 (s, C-2), 134.8 (s, C-3), 178.2 (s, C-4), 161.8 (s, C-5), 93.3 (d, C-6), 164.5 (d, C-7), 98.4 (d, C-8), 157.8 (s, C-9), 104.4 (s, C-10), 121.5 (s, C-1′), 115.0 (d, C-2′), 145.0 (s, C-3′), 148.4 (s, C-4′), 115.5 (d, C-5′), 121.4 (d, C-6′), 102.1 (d, C-1″), 70.7 (d, C-2″), 70.6 (d, C-3″), 71.8 (d, C-4″), 70.4 (d, C-5″), 16.4 (q, C-6″).

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