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滇南羊耳菊乙酸乙酯部位化学成分研究

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摘　要:从滇南羊耳菊(*Inula wissmanniana*)地上部分的乙酸乙酯部位分离得到16个化合物,包括6个黄酮类,5个苯丙素类和5个其它芳香类化合物,经波谱数据分析鉴定为木犀草素(**1**),3-甲氧基槲皮素(**2**),5,6,4′-三羟基-3,7-二甲氧基黄酮(**3**),洋艾素(**4**),紫杉叶素(**5**),二氢山奈酚(**6**),3,4-二-*O*-咖啡酰奎宁酸(**7**),3,5-二-*O*-咖啡酰奎宁酸(**8**),*C*-veratroylglycol(**9**),2,3-dihydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone(**10**),咖啡酸(**11**),邻苯二甲酸二丁酯(**12**),3,4-二羟基苯甲酸(**13**),3-羟基-4-甲氧基苯甲酸(**14**),对羟基苯甲酸(**15**)和香兰素(**16**)。所有化合物均为首次从该植物中分离得到。

关键词:滇南羊耳菊;旋覆花属;黄酮;苯丙素;芳香化合物

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Chemical Constituents from the Ethyl Acetate Portion of *Inula wissmanniana*

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Abstract: Sixteen compounds were isolated from the ethyl acetate portion of the aerial part of *Inula wissmanniana*, including six flavonoids, five phenylpropanoids, and five other aromatic compounds. On the basis of spectral data, their structures were identified as luteolin (**1**), 3-*O*-methylquercetin (**2**), 5,6,4′-trihydroxy-3,7-dimethoxyflavone (**3**), artemetin (**4**), taxifolin (**5**), dihydrokaempferol (**6**), 3,4-di-*O*-caffeoyl quinic acid (**7**), 3,5-di-*O*-caffeoylquinic acid (**8**), *C*-veratroylglycol (**9**), 2,3-dihydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone (**10**), caffeic acid (**11**), dibutylphthalate (**12**), 3,4-dihydroxybenzoic acid (**13**), 3-hydroxy-4-methoxybenzoic acid (**14**), *p*-hydroxybenzoic acid (**15**) and vanillin (**16**). All the compounds were isolated from this plant for the first time.

Key words: *Inula wissmanniana*; *Inula*; flavonoids; phenylpropanoids; aromatic compounds

Introduction

Inula wissmanniana, a suffrutescent plant belonging to the Asteraceae family, mainly distributed in the south of Yunnan province of China, growing at 1200-1650 m above sea level [1]. So far, no chemical constituents have been reported from *I. wissmanniana*. In this study, we isolated and identified sixteen compounds from an ethyl acetate (EtOAc) extract of the aerial parts of this plant, including luteolin (**1**), 3-*O*-methylquercetin (**2**), 5,6,4′-trihydroxy-3,7-dimethoxyflavone (**3**), artemetin (**4**), taxifolin (**5**), dihydrokaempferol (**6**), 3,4-di-*O*-caffeoyl quinic acid (**7**), 3,5-di-*O*-caffeoylquinic acid (**8**), *C*-veratroylglycol (**9**), 2,3-dihydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone (**10**), caffeic acid (**11**), dibutylphthalate (**12**), 3,4-dihydroxybenzoic acid (**13**), 3-hydroxy-4-methoxybenzoic acid (**14**), *p*-hydroxybenzoic acid (**15**) and vanillin (**16**). All the compounds were isolated from this plant for the first time.

Experimental

General procedures

The normal phase silica gel (100-200, 200-300 mesh, Yantai, China), MCI gel (CHP20P 75-150 μm, Mitsubishi Chemical Co., Japan), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden) were used for column chromatography, and precoated silica HS-

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GF_{254} plates were used for TLC (Yantai, China). HPLC were performed with SHIMADZU LC 2010AHT, Agilent Technologies 1200 series, semipreparative HPLC was obtained on a SHIMADZU LC-6AD series using a Zorbax-SB-C_{18} (5 μm, 9.4 × 250 nm). The ESI-MS were measured on an Agilent 1100 series mass spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker DRX-400 spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Chemical shift (δ) were given in ppm relative to TMS as internal reference and coupling constants (J) in Hz.

Plant material

The aerial parts of *I. wissmanniana* were collected from Pingbian county of Yunnan Province, China, in August 2010 and identified by Prof. Zhang Han-Ming, Department of Pharmacognosy, School of Pharmacy, Second Military Medical University. A voucher specimen has been deposited at School of Pharmacy (NO. 201008DNYEJ) Shanghai Jiao Tong University.

Extraction and isolation

The air-dried and powdered aerial parts of *I. wissmanniana* (30.0 kg) were extracted with 95% EtOH for three times at room temperature, the extracts were combined and concentrated to yield a residue (631.4 g). The residue was suspended in H_2O (6.0 L) and then partitioned successively with petroleum ether (12.0 L ×5), CH_2Cl_2 (12.0 L ×5), EtOAc (12.0 L ×5) and *n*-butanol (12.0 L ×5), giving 133.2 g, 179.6 g, 28.1 g and 35.2 g, respectively. The EtOAc fraction was chromatographed on a silica gel column eluting with CH_2Cl_2-MeOH (100∶1 to 0∶100) gradient to obtain six fractions (Fr. 1-Fr. 6). Six fractions were all applied to MCI gel column chromatography (MeOH-H_2O, 9∶1). Fr. 2 (2.1 g) was further subjected to a silica gel column and eluted with CH_2Cl_2-MeOH (100∶1 to 20∶1) to give compound **4** (20.1 mg). Fr. 3 (3.1 g) was separated by Sephadex LH-20 (MeOH) to give **4** subfractions. The subfraction 2 was submitted to preparative HPLC (RP_{18}, 210 nm, CH_3CN-H_2O-HCOOH, 17∶83∶0.1), yielding compounds **9** (3.8 mg, t_R = 13.4 min), **10** (1.6 mg, t_R = 14.3 min), **14** (50.8 mg, t_R = 25.4 min) and **15** (23.0 mg, t_R = 35.5 min). The subfraction 4 was submitted to preparative HPLC (RP_{18}, 210 nm, MeOH-H_2O, 80∶20) to obtain **12** (9.0 mg, t_R = 24.0 min). Fr. 4 (3.7 g) was subjected to Sephadex LH-20 (MeOH) to give 5 subfractions. The subfraction 3 was separated by preparative HPLC (RP_{18}, 210 nm, CH_3CN-H_2O-HCOOH, 17∶83∶0.1) to give compounds **3** (11.1 mg, t_R = 72.1 min), **11** (29.0 mg, t_R = 19.3 min), **13** (17.1 mg, t_R = 12.5 min) and **16** (21.6 mg, t_R = 41.8 min), the subfraction 4 was separated by preparative HPLC (RP_{18}, 210 nm, CH_3CN-H_2O, 20∶80) to yield compounds **1** (102.2 mg, t_R = 51.3 min), **2** (5.0 mg, t_R = 97.2 min), **5** (58.4 mg, t_R = 27.0 min) and **6** (13.3 mg, t_R = 35.2 min). Compounds **7** (37.7 mg, t_R = 60.5 min) and **8** (25.8 mg, t_R = 78.6 min) were obtained after the purification of Fr. 6 (5.2 g) by Sephadex LH-20 (MeOH) and preparative HPLC (RP_{18}, 210 nm, CH_3CN-H_2O-HCOOH, 20∶80∶0.1).

Structure identification

Luteolin (**1**) $C_{15}H_{10}O_6$, yellow amorphous powder, ESI-MS (positive) *m/z* 309 $[M + Na]^+$, ESI-MS (negative) *m/z* 285 $[M-H]^-$; ^1H NMR (400 MHz, DMSO-d_6) δ: 12.94 (1H, s, 5-OH), 7.40 (1H, brs, H-6′), 7.38 (1H, s, H-2′), 6.87 (1H, d, J = 8.1 Hz, H-5′), 6.64 (1H, s, H-3), 6.43 (1H, d, J = 1.4 Hz, H-8), 6.17 (1H, d, J = 1.4 Hz, H-6); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 181.7 (C-4), 164.1 (C-7), 163.9 (C-2), 161.5 (C-9), 157.3 (C-5), 149.7 (C-4′), 145.8 (C-3′), 121.5 (C-1′), 119.0 (C-6′), 116.1 (C-5′) 113.4 (C-2′), 103.7 (C-10), 102.9 (C-3), 98.9 (C-6), 93.9 (C-8). The NMR and MS data were in accordance with those reported in the literature [2], and identified 1 as luteolin.

3-*O*-Methylquercetin (**2**) $C_{16}H_{12}O_7$, yellow amorphous powder, ESI-MS (positive) *m/z* 339 $[M + Na]^+$, ESI-MS (negative) *m/z* 315 $[M-H]^-$; ^1H NMR (400 MHz, CD_3OD) δ: 7.61 (1H, s, H-2′), 7.52 (1H, d, J = 8.5 Hz, H-6′), 6.89 (1H, d, J = 8.5 Hz, H-5′), 6.39 (1H, s, H-8), 6.19 (1H, brs, H-6), 3.77 (3H, s, 3-OCH_3); ^{13}C NMR (100 MHz, CD_3OD) δ: 180.0 (C-4), 166.0 (C-7), 163.1 (C-5), 158.4 (C-9), 158.0 (C-2), 150.0 (C-4′), 146.5 (C-3′), 139.5 (C-3), 122.9 (C-1′), 122.3 (C-6′), 116.5

(C-2′), 116.4 (C-5′), 105.9 (C-10), 99.8 (C-6), 94.6 (C-8), 60.5 (3-OCH_3). The NMR and MS data were in accordance with those reported in the literature [3], and identified **2** as 3-*O*-methylquercetin.

5,6,4′-Trihydroxy-3,7-dimethoxyflavone (**3**) $C_{17}H_{14}O_7$, yellow needle crystals, ESI-MS (positive) *m/z* 353 $[M+Na]^+$, ESI-MS (negative) *m/z* 329 $[M-H]^-$; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.38 (1H, brs, 5-OH), 7.96 (2H, d, J = 8.6 Hz, H-2′,6′), 6.94 (2H, d, J = 8.6 Hz, H-3′,5′), 6.85 (1H, s, H-8), 3.90 (3H, s, 7-OCH_3), 3.79 (3H, s, 3-OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 178.1 (C-4), 160.3 (C-4′), 155.7 (C-2), 154.5 (C-7), 148.9 (C-9), 145.7 (C-5), 137.5 (C-3), 130.0 (C-2′,6′), 129.6 (C-6), 120.7 (C-1′), 115.7 (C-3′,5′), 105.6 (C-10), 90.9 (C-8), 59.7 (3-OCH_3), 56.3 (7-OCH_3). The NMR and MS data were in accordance with those reported in the literature [4], and identified **3** as 5,6,4′-trihydroxy-3,7-dimethoxyflavone.

Artemetin (**4**) $C_{20}H_{20}O_8$, yellow amorphous powder, ESI-MS (positive) *m/z* 411 $[M+Na]^+$, ESI-MS (negative) *m/z* 387 $[M-H]^-$; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.6 (1H, brs, 5-OH), 7.74 (1H, dd, J = 8.6, 1.8 Hz, H-6′), 7.67 (1H, d, J = 1.8 Hz, H-2′), 7.16 (1H, d, J = 8.6 Hz, H-5′), 6.94 (1H, s, H-8), 3.94, 3.83, 3.70 (each 3H, s, 3 × -OCH_3), 3.87 (6H, s, 2 × -OCH_3); ^{13}C NMR (400 MHz, DMSO-d_6) δ: 178.3 (C-4), 158.7 (C-7), 155.5 (C-9), 151.8 (C-2), 151.6 (C-5), 151.3 (C-4′), 148.5 (C-3′), 138.1 (C-3), 131.6 (C-6), 122.1 (C-1′), 122.0 (C-6′), 111.6 (C-5′), 111.3 (C-2′), 105.6 (C-10), 91.5 (C-8), 60.0, 59.8, 56.5, 55.7, 55.6 (6 × -OCH_3). The NMR and MS data were in accordance with those reported in the literature [5], and identified **4** as artemetin.

Taxifolin (**5**) $C_{15}H_{12}O_7$, yellow amorphous powder, ESI-MS (positive) *m/z* 327 $[M+Na]^+$, ESI-MS (negative) *m/z* 303 $[M-H]^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 6.97 (1H, s, H-2′), 6.84 (1H, d, J = 8.0 Hz, H-5′), 6.79 (1H, d, J = 8.0 Hz, H-6′), 5.91 (1H, s, H-8), 5.87 (1H, s, H-6), 4.89 (1H, d, J = 11.4 Hz, H-2), 4.49 (1H, d, J = 11.4 Hz, H-3); ^{13}C NMR (100 MHz, CD_3OD) δ: 198.2 (C-4), 168.6 (C-7), 164.4 (C-5), 164.3 (C-9), 147.0 (C-4′), 146.2 (C-3′), 129.8 (C-1′), 120.9 (C-6′), 116.1 (C-2′), 115.9 (C-5′), 101.8 (C-10), 97.3 (C-6), 96.3 (C-8), 84.9 (C-2), 73.5 (C-3). The NMR and MS data were in accordance with those reported in the literature [6], and identified **5** as toxifolin.

Dihydrokaempferol (**6**) $C_{15}H_{12}O_6$, yellow needle crystals, ESI-MS (positive) *m/z* 311 $[M+Na]^+$, ESI-MS (negative) *m/z* 287 $[M-H]^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.34 (2H, d, J = 8.6 Hz, H-2′, 6′), 6.83 (2H, d, J = 8.6 Hz, H-3′,5′), 5.92 (1H, s, H-8), 5.88 (1H, s, H-6), 4.97 (1H, d, J = 11.4 Hz, H-2), 4.53 (1H, d, J = 11.4 Hz, H-3); ^{13}C NMR (100 MHz, CD_3OD) δ: 198.5 (C-4), 168.8 (C-5), 164.6 (C-9), 159.2 (C-4′), 130.4 (C-2′, 6′), 129.3 (C-1′), 116.2 (C-3′, 5′), 101.9 (C-10), 97.4 (C-6), 96.3 (C-8), 85.0 (C-2), 73.7 (C-3). The NMR and MS data were in accordance with those reported in the literature [7], and identified **6** as dihydrokaempferol.

3,4-di-*O*-Caffeoyl quinic acid (**7**) $C_{25}H_{24}O_{12}$, yellow amorphous powder, ESI-MS (negative) *m/z* 515 $[M-H]^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.62 (1H, d, J = 15.0 Hz, H-7′), 7.53 (1H, d, J = 15.0 Hz, H-7″), 7.03 (2H, s, H-2′, 2″), 6.91 (2H, d, J = 7.0 Hz, H-6′, 6″), 6.77 (2H, d, J = 8.1 Hz, H-5′, 5″), 6.30 (1H, d, J = 14.0 Hz, H-8″), 6.21 (1H, d, J = 14.0 Hz, H-8′), 5.67 (1H, m, H-3), 4.32 (1H, m, H-5), 3.73 (1H, m, H-4), 2.00? 2.31 (4H, m, H-2, 6); ^{13}C NMR (100 MHz, CD_3OD) δ: 168.5 (C-9′), 168.3 (C-9″), 149.5 (C-4′, 4″), 147.7 (C-7′, 7″), 147.5 (C-3″), 146.6 (C-3′), 127.7 (C-1″), 127.6 (C-1′), 123.1 (C-6′, 6″), 116.4 (C-5′, 5″), 115.2 (C-8′, 8″), 114.6 (C-2′, 2″), 75.9 (C-4), 69.6 (C-3), 69.1 (C-5), 39.5 (C-6), 38.3 (C-2). The NMR and MS data were in accordance with those reported in the literature [8], and identified **7** as 3,4-di-*O*-caffeoyl quinic acid.

3,5-di-*O*-Caffeoyl quinic acid (**8**) $C_{25}H_{24}O_{12}$, yellow amorphous powder, ESI-MS (negative) *m/z* 515 $[M-H]^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.63 (1H, d, J = 15.6 Hz, H-7″), 7.57 (1H, t, J = 15.6 Hz, H-

7′),7.06 (2H,brs,H-2′,2″),6.96 (2H,d,J =8.0 Hz,H-6′,6″),6.77 (2H,d,J =8.0 Hz,H-5′,5″),6.35 (1H,d,J =15.8 Hz,H-8″),6.26 (1H,d,J =15.8 Hz,H-8′),5.42 (2H,brs,H-3,5),3.96 (1H,brs,H-4),2.02-2.23 (4H,m,H-2,6);^{13}C NMR (100 MHz,CD_3OD) δ:168.9 (C-9″),168.4 (C-9′),149.6 (C-4″),149.5 (C-4′),147.9 (C-3″),147.1 (C-7″),146.8 (C-3′,7′),127.9 (C-1″),127.8 (C-1′),123.1 (C-6″),123.0 (C-6′),116.5 (C-5″,8″),115.6 (C-5′),115.3 (C-2″),115.2 (C-2′),115.1 (C-8′),74.7 (C-1),72.5 (C-3),72.1 (C-5),70.6 (C-4),38.2 (C-2),36.3 (C-6). The NMR and MS data were in accordance with those reported in the literature [9], and identified **8** as 3,5-di-*O*-caffeoyl quinic acid.

***C*-Veratroylglycol (9)** $C_{10}H_{12}O_5$, brown amorphous powder, ESI-MS (positive) m/z 235 [M+Na]$^+$, ESI-MS (negative) m/z 211 [M-H]$^-$; ^{1}H NMR (400 MHz,CD_3OD) δ: 7.59 (1H,s,H-2),7.57 (1H,d,J =8.5 Hz,H-6),6.87 (1H,d,J =8.5 Hz,H-5),5.11 (1H,t,J =4.8 Hz,H-8),3.88 (3H,s,3-OCH_3),3.86 (1H,m,H-9α),3.72 (1H,m,H-9β);^{13}C NMR (100 MHz,CD_3OD) δ: 199.7 (C-7),153.9 (C-4),149.3 (C-3),128.0 (C-1),125.1 (C-6),115.9 (C-5),112.5 (C-2),75.5 (C-8),66.2 (C-9),56.5 (3-OCH_3). The NMR and MS data were in accordance with those reported in the literature [10], and identified **9** as *C*-veratroylglycol.

2, 3-Dihydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl)-1-propanone (10) $C_{11}H_{14}O_6$, white amorphous powder, ESI-MS (positive) m/z 265 [M+Na]$^+$, ESIMS (negative) m/z 241 [M-H]$^-$; ^{1}H NMR (400 MHz,CD_3OD) δ: 7.34 (2H,s,H-2′,6′),5.11 (1H,dd,J =5.0,4.0 Hz,H-2),3.90 (6H,s,3′,5′-OCH_3),3.85 (1H,dd,J =11.6,4.0 Hz,H-3α),3.73 (1H,dd,J =11.6,5.0 Hz,H-3β);^{13}C NMR (100 MHz,CD_3OD) δ: 199.6 (C-1),149.5 (C-3′,5′),107.9 (C-2′,6′),75.6 (C-2),66.3 (C-3),57.0 (3′,5′-OCH_3). The NMR and MS data were in accordance with those reported in the literature [11], and identified **10** as 2,3-dihydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone.

Caffeic acid (11) $C_9H_8O_4$, brown amorphous powder, ESI-MS (positive) m/z 203 [M+Na]$^+$, ESI-MS (negative) m/z 179 [M-H]$^-$; ^{1}H NMR (400 MHz,CD_3OD) δ: 7.52 (1H,d,J =15.6 Hz,H-1′),7.03 (1H,s,H-2),6.91 (1H,d,J =8.1 Hz,H-6),6.76 (1H,d,J =8.1 Hz,H-5),6.21 (1H,d,J =15.6 Hz,H-2′);^{13}C NMR (100 MHz,CD_3OD) δ: 171.4 (C-3′),149.4 (C-4),147.0 (C-3),146.7 (C-2),127.8 (C-1),122.8 (C-5),116.5 (C-6),115.7 (C-1′),115.1 (C-2′). The NMR and MS data were in accordance with those reported in the literature [12], and identified **11** as caffeic acid.

Dibutylphthalate (12) $C_{16}H_{22}O_4$, pink oil, ESI-MS (positive) m/z 301 [M+Na]$^+$; ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.71 (2H,dd,J =5.7,3.3 Hz,H-3,6),7.60 (2H,dd,J =5.7,3.3 Hz,H-4,5),4.28 (4H,t,J =6.6 Hz,H-8,8′),1.73 (4H,m,J =6.6 Hz,H-9,9′),1.44 (4H,m,J =7.6 Hz,H-10,10′),0.97 (6H,t,J =7.6 Hz,H-11,11′);^{13}C NMR (CD_3OD,100 MHz) δ:169.3 (C-7,7′),133.6 (C-1,2),132.3 (C-4,5),129.9 (C-3,6),66.7 (C-8,8′),31.7 (C-9,9′),20.2 (C-10,10′),14.0 (C-11,11′). The NMR and MS data were in accordance with those reported in the literature [13], and identified **12** as dibutylphthalate.

3,4-Dihydroxybenzoic acid (13) $C_7H_6O_4$, white needle crystals, ESI-MS (positive) m/z 177 [M+Na]$^+$, ESI-MS (negative) m/z 153 [M-H]$^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.43 (1H,s,H-2),7.41 (1H,d,J =10.0 Hz,H-6),6.78 (1H,d,J =10.0 Hz,H-5);^{13}C NMR (100 MHz,CD_3OD) δ:170.2 (C=O),151.5 (C-4),146.0 (C-3),123.9 (C-2),117.7 (C-6),115.8 (C-5). The NMR and MS data were in accordance with those reported in the literature [14], and identified **13** as 3,4-dihydroxybenzoic acid.

3-Hydroxy-4-methoxybenzoic acid (14) $C_8H_8O_4$, white needle crystals, ESI-MS (positive) m/z 191 [M+Na]$^+$, ESI-MS (negative) m/z 167 [M-H]$^-$; ^{1}H NMR (400 MHz,CD_3OD) δ:7.56 (1H,brs,H-2,),7.55 (1H,brs,H-6),6.83 (1H,d,J =8.3 Hz,H-5),3.89 (3H,s,4-OCH_3);^{13}C NMR (100 MHz, CD_3OD) δ:152.5 (C-4),148.7 (C-3),125.3 (C-6),115.8 (C-2),113.9 (C-5),56.4 (4-OCH_3). The

NMR and MS data were in accordance with those reported in the literature [15], and identified **14** as 3-hydroxy-4-methoxybenzoic acid.

***p*-Hydroxybenzoic acid (15)** $C_7H_6O_3$, white amorphous powder, ESI-MS (negative) *m/z* 137 [M-H]$^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.86 (2H, d, *J* = 8.0 Hz, H-2, 6), 6.80 (2H, d, *J* = 8.0 Hz, H-3, 5); ^{13}C NMR (100 MHz, CD_3OD) δ: 170.8 (1-COOH), 163.6 (C-4), 133.3 (C-2, 6), 123.5 (C-1), 116.3 (C-3, 5). The NMR and MS data were in accordance with those reported in the literature [16], and identified **15** as *p*-hydroxybenzoic acid.

Vanillin (16) $C_8H_8O_3$, white needle crystal, ESI-MS (negative) *m/z* 151 [M-H]$^-$; ^{1}H NMR (CD_3OD, 400 MHz) δ: 9.63 (1H, s, 1-CHO), 7.38 (2H, brs, H-2, 6), 6.83 (1H, d, *J* = 8.0 Hz, H-5), 3.87 (3H, s, 3-OCH_3); ^{13}C NMR (CD_3OD, 400 MHz) δ: 190.7 (1-CHO), 151.7 (C-4), 147.2 (C-3), 129.9 (C-1), 127.3 (C-6), 114.4 (C-5), 108.9 (C-2), 56.1 (3-OCH_3). The NMR and MS data were in accordance with those reported in the literature [17], and identified **16** as vanillin.

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