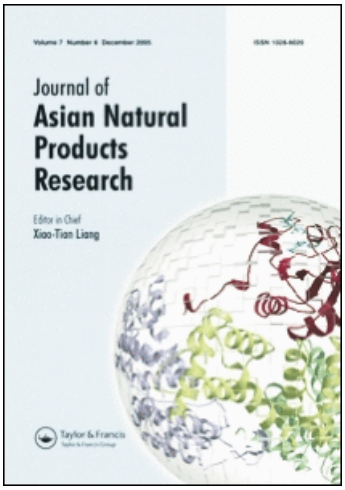


**Journal of Asian Natural Products Research**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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Online publication date: 09 September 2010

*Journal of Asian Natural Products Research*, 2002 VOL. 4 (4), pp. 287–295





# POLYPHENOLIC COMPOUNDS FROM THE LEAVES OF *KOELREUTERIA PANICULATA* LAXM

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*(Received 1 March 2002; Revised 10 April 2002; In final form 25 April 2002)*

From the fresh leaves of *Koelreuteria paniculata* Laxm (Sapindaceae), four new compounds, named ethyl *p*-trigallate (**1**), 3″-*O*-galloyl-4′-*O*-galloyl-4-*O*-galloyl-gallic acid (**2**), ethyl *p*-heptagallate (**3**) and 3″-galloylquercitrin (**4**), together with 12 known compounds namely catechin (**5**), galloylepicatechin (**6**), isorhamnetin (**7**), kaempferol-3-*O*-arabinopyranoside (**8**), quercetin-3′-*O*-β-D-arabinopyranoside (**9**), quercitrin (**10**), methyl *p*-digallate (**11**), methyl *m*-digallate (**12**), *p*-digalloyl acid (**13**), *m*-digalloyl acid (**14**), hyperin (**15**) and kaempferol-3-*O*-α-L-rhamnoside (**16**) were isolated by extensive column chromatographic separation. Their structures were elucidated on the basis of chemical and spectroscopic methods. Compound **9** was not reported previously with pyranoside of arabinose at C-3′. Compounds **4** and **9** possessed the activity for PTK inhibition.

*Keywords*: *Koelreuteria paniculata*; Leaves; Galloyl derivatives; Flavonoids

## INTRODUCTION

*Koelreuteria paniculata* Laxm (Sapindaceae) is widely distributed in Northern China. Local people use the seeds as insecticides and the leaves as anti-fungal and anti-bacterial agents [1]. Recent reports showed that the crude extracts of this plant possessed anti-tumor and anti-oxidation activities [2,3]. In our previous work, a number of gallate derivatives [4], cyanolipids [5] and flavonoids [6] have been isolated. In the systematic study on the bioactive secondary metabolites from the plant, the fresh leaves were collected in the mountain area close to Beijing suburbs in autumn. The PTK bioassay for directing the isolation of PTK inhibitors from the ethanol extracts by extensive column chromatography led to the isolation of two types of compounds. One was related to galloyl derivatives such as ethyl *p*-trigallate (**1**), 3″-*O*-galloyl-4′-*O*-galloyl-4-*O*-galloyl-gallic acid (**2**), ethyl *p*-heptagallate (**3**), 3″-galloylquercitrin (**4**), galloylepicatechin (**6**) [7], methyl *p*-digallate (**11**) [8], methyl *m*-digallate (**12**) [8], *p*-digalloyl acid (**13**) [4], *m*-digalloyl acid (**14**) [4], and the other belonged to flavonoids: catechin (**5**) [7], isorhamnetin (**7**) [9], kaempferol-3-*O*-arabinopyranoside (**8**) [10], quercetin-3′-*O*-β-arabinopyranoside

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ISSN 1028-6020 print/ISSN 1477-2213 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/1028602021000049087

(**9**), quercitrin (**10**) [11], hyperin (**15**) [12] and kaempferol-3-*O*-α-L-rhamnoside (**16**) [13]. The structures of the known compounds were identified by comparative analysis of their spectra, chemical and physical properties with those reported in literatures. The aim of this report is to describe the structure elucidation for the new compounds.

## RESULTS AND DISCUSSION

From the ethanol extracts of the leaves, by repeated flash chromatography on silica gel column and Sephadex LH-20 as well as ODS HPLC chromatography, two classes of compounds, flavonoids and galloyl derivatives, were isolated.

Compound **1** was obtained as a white amorphous powder. Its molecular formula $C_{23}H_{18}O_{13}$ was deduced from a quasimolecular peak of positive FABMS spectrum at *m/z* 503 [M + 1] and 525 [M + Na] in association with its $^{13}C$ NMR spectrum. The positive reaction showing a dark blue color with $FeCl_3$ was characteristic of the phenolic group. IR absorptions at 3270(br), 1703, 1610 $cm^{-1}$ supported the presence of a phenolic group and suggested the presence of carbonyl and aromatic groups. The $^1H$ and $^{13}C$ NMR spectra (Table I) closely resembled those of ethyl *p*-gallate [4], indicating that **1** was a galloyl derivative. Compound **1** presented one more galloyl residue than ethyl *p*-gallate by direct comparison of both molecular constituents along with the $^{13}C$ NMR spectrum. The linkage of the galloyl residues was proposed to be attached at C-4 and C-4′ successively according to the double intensity signals for each aromatic protons. The FABMS spectrum showed fragments at *m/z* 153, 305, 457, and supported the evidence of linkage. An ethyl group ($\delta$ 1.25, t, $J = 6.9$ Hz; 4.17, q, $J = 6.9$ Hz and $\delta$ 60.05, t; 14.28.q) was deduced to form an ester with the terminal galloyl residue due to the correlation of methene proton signal $\delta$ 4.17(q) with $\delta$ 167.52(s) in HMBC spectrum. Thus, the structure of **1** was determined as ethyl *p*-trigallate. Its $^{13}C$ NMR data are assigned in Table I (Fig. 1).

Compound **2** was obtained as a white amorphous powder. Its molecular formula $C_{28}H_{18}O_{17}$ was obtained by a quasimolecular peak of positive FABMS spectrum at *m/z* 627 [M + 1] and 665 [M + K] in association with its $^{13}C$ NMR spectrum. The positive reaction to give a dark blue color with $FeCl_3$ implied the presence of a phenolic group. IR absorptions at 3360(br), 1710, 1616 $cm^{-1}$ suggested the presence of hydroxyls, carbonyl and aromatic groups. The $^1H$ and $^{13}C$ NMR spectra showed signals typical of the galloyl pattern. The $^1H$ NMR spectrum exhibited equivalent signals at $\delta$ 6.99(s, 2H), 7.04(s, 4H), as well as $\delta$ 7.30(d, $J = 2.0$ Hz) and 7.09(d, $J = 2.0$ Hz), indicating the existence of four galloyl residues, two for *para* substitutions and one for *meta* substitution. The linkage of the galloyl residues was further confirmed by chemical conversion. Compound **2** and Dowex $50H^+$ were stirred in dry ethanol at room temperature under argon for 48 h to afford an ethylated product (Fig. 2) which was hydrolyzed in acetone with aqueous LiOH to produce a mixture in which **1** was observed by its HPLC-ESIMS spectrum. Therefore, **2** was elucidated to be 3″-*O*-galloyl-4′-*O*-galloyl-4-*O*-galloyl-galloyl acid. Its $^{13}C$ NMR data are assigned in Table I.

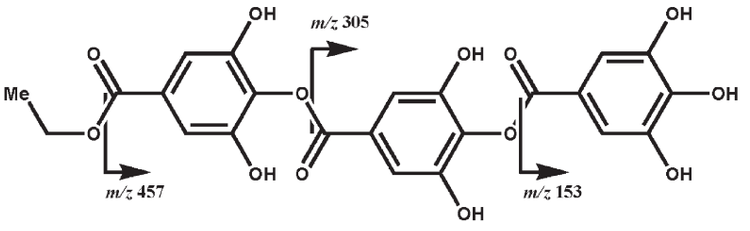
Compound **3** was a white amorphous powder. Its quasimolecular peaks at *m/z* 1111 [M + 1] and 1149 [M + K] in positive FABMS spectrum along with $^{13}C$ NMR spectrum were compatible with the molecular formula $C_{51}H_{34}O_{29}$. Compound **3** also showed a positive reaction with $FeCl_3$ as described for **1** and **2**. Its IR, $^1H$ and $^{13}C$ NMR spectra (Table I) closely resembled those of **1** with the exception of four additional galloyl residues which were observed through the obvious fragments at *m/z* 153, 197, 305, 457, 609, 761, 913, 1065 in the MS/MS ESIMS spectrum while selected *m/z* 1111 for fragmentation. The linkage of

TABLE I $^{13}C$ NMR data of compounds **1**–**3**

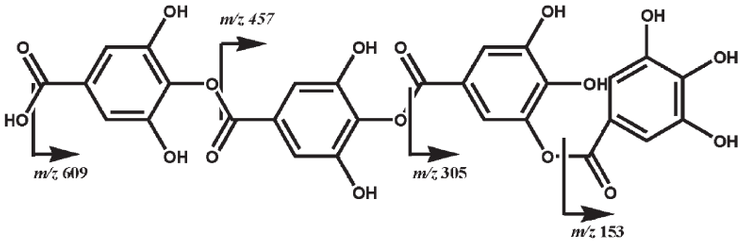
| C | 1 | 2 | 3 |
|---|---|---|---|
| Galloyl | | | |
| CO | 167.52,s | 167.50,s | 165.42,s |
| 1 | 127.62,s | 127.35,s | 127.51,s |
| 2,6 | 108.50,d | 108.70,d | 108.09,d |
| 3,5 | 150.72,s | 150.47,s | 150.73,s |
| 4 | 131.41,s | 132.10,s | 131.56,s |
| galloyl | | | |
| CO′ | 164.87,s | 164.22,s | 164.74,s |
| 1′ | 120.84,s | 121.10,s | 119.62,s |
| 2′,6′ | 108.63,d | 108.73,d | 108.51,d |
| 3′,5′ | 150.44,s | 149.50,s | 150.54,s |
| 4′ | 131.02,s | 132.32,s | 131.56,s |
| galloyl | | | |
| CO″ | 165.23,s | 164.60,s | 164.19,s |
| 1″ | 119.35,s | 117.70,s | 119.32,s |
| 2″ | 109.28,d | 114.12,d | 108.78,d |
| 3″ | 145.59,s | 145.80,s | 149.32,s |
| 4″ | 138.37,s | 142.22,s | 131.37,s |
| 5″ | 145.59,s | 138.23,s | 149.32,s |
| 6″ | 109.28,d | 116.21,d | 108.78,d |
| galloyl | | | |
| CO‴ | | 164.44,s | 164.87,s |
| 1‴ | | 118.11,s | 119.61,s |
| 2‴,6‴ | | 107.89,d | 108.59,d |
| 3‴,5‴ | | 145.56,s | 148.12,s |
| 4‴ | | 138.32,s | 133.31,s |
| galloyl | | | |
| CO′′′′ | | | 163.53,s |
| 1′′′′ | | | 118.38,s |
| 2′′′′,6′′′′ | | | 108.09,d |
| 3′′′′,5′′′′ | | | 147.10,s |
| 4′′′′ | | | 132.11,s |
| galloyl | | | |
| CO′′′′′ | | | 163.84,s |
| 1′′′′′ | | | 118.08,s |
| 2′′′′′,6′′′′′ | | | 109.10,d |
| 3′′′′′,5′′′′′ | | | 148.95,s |
| 4′′′′′ | | | 133.00,s |
| galloyl | | | |
| CO′′′′′′ | | | 164.73,s |
| 1′′′′′′ | | | 118.48,s |
| 2′′′′′′,6′′′′′′ | | | 108.54,d |
| 3′′′′′′,5′′′′′′ | | | 145.73,s |
| 4′′′′′′ | | | 138.79,s |
| Me | 14.28,q | | 14.24,q |
| $CH_2$ | 60.05,t | | 60.08,t |

the galloyl residues was proposed to attach at a *para* position successively due to the equivalent signals for the aromatic protons. An ethyl group ($\delta$ 1.27, t, $J = 7.2$ Hz; 4.24, q, $J = 7.2$ Hz and 14.24.q; $\delta$ 60.08, t) was proved to form an ester with the terminal galloyl residue due to the correlation of the methene proton signal $\delta$ 4.24(q) with $\delta$ 165.42(s) in HMBC spectrum. The structure of **3** was thus determined as ethyl *p*-heptgallate. Its $^{13}C$ NMR data were assigned in Table I.

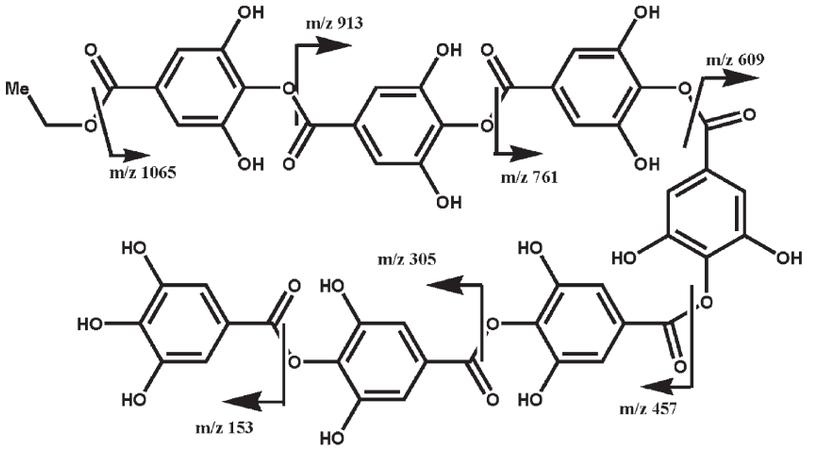
Compound **4** was a yellow amorphous powder, and appeared pale yellow at 254 nm, purple at 366 nm and yellow under UV/$NH_3$ on a TLC plate indicating it to be a flavonoid. The IR absorptions at 3710, 1755, 1705, and 1620 $cm^{-1}$ suggested the presence of hydroxyl,




**1** *m/z* 503 [M+1]




**2** *m/z* 627 [M+1]




**3** *m/z* 1111 [M+1]

FIGURE 1 Major MS fragments of compounds **1**–**3**.

carbonyl and aromatic functions. The $^1$H NMR spectrum showed $\delta$ 12.62(br, OH-5), 6.12(d, $J = 2.0$ Hz, H-6), 6.39(d, $J = 2.0$ Hz, H-8), 7.32(dd, $J = 8.1$, 2.2 Hz, H-6′), 7.29(d, $J = 2.2$ Hz, H-2′) and 6.87(d, $J = 8.1$ Hz, H-5′), characteristic of a quercetin skeleton, together with an anomeric proton $\delta$ 5.20(br, H-1″) and methyl $\delta$ 0.88(d, $J = 6.0$ Hz, H-6″)

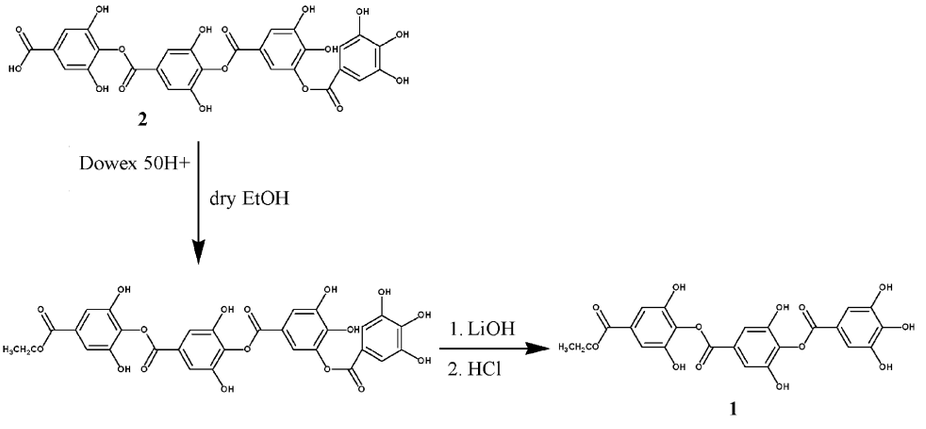



FIGURE 2 Chemical conversion of **2** to **1**.



indicating the presence of a rhamnose moiety. Furthermore, an additional aromatic equivalent signal observed as singlet at $\delta$ 7.03(s, 2H) was assigned to the H-2‴ and H-6‴ of the galloyl residue, which was supported by direct comparison of its $^{1}$H and $^{13}$C NMR data with those of hyperin-2″-gallate [4]. The downfield shifted signal of H-3″ ($\delta$ 5.00, dd, $J = 3.3$, 9.3 Hz) assigned by 1D TOCSY spectrum led us to consider that the galloyl moiety was linked to C-3″ of rhamnose residue. The correlation of the anomeric proton H-1″ to $\delta$ 134.53 (s, C-3) in the HMBC spectrum suggests connection of the rhamnose residue to C-3 of quercetin. From the above experimental results, the chemical structure of **4** was proposed as quercitin-3-*O*-(3″-*O*-galloyl)-α-L-rhamnopyranoside.

Compound **9** was a yellow amorphous powder, and appeared pale yellow at 254 nm, purple at 366 nm and yellow under UV/$NH_3$ on a TLC plate indicating it to be a flavonoid. Its molecular formula $C_{20}H_{18}O_{11}$ was proposed on the basis of the molecular ion *m/z* 434 in its EIMS spectrum in association with its $^{13}$C NMR spectrum. The IR absorptions at 3542, 1710, 1701, and 1624 $cm^{-1}$ suggested the presence of hydroxyl, carbonyl and aromatic functions. The $^{1}$H NMR spectrum showed $\delta$ 6.27(d, $J = 3.5$ Hz, H-6), 6.46(d, $J = 3.5$ Hz, H-8), 7.67(dd, $J = 8.5$, 2.0 Hz, H-6′), 7.84(d, $J = 2.0$ Hz, H-2′) and 6.96(d, $J = 8.5$ Hz, H-5′), indicating a quercetin skeleton. Moreover, 1D TOCSY exhibited the correlated proton signals at $\delta$ 5.23(d, $J = 6.5$ Hz, H-1″), 3.99(dd, $J = 6.5$, 8.5 Hz, H-2″), 3.73(dd, $J = 3.0$, 8.5 Hz, H-3″), 3.90(ddd, $J = 3.0$, 4.0, 4.5 Hz, H-4″), 3.92(dd, $J = 4.0$, 11.0 Hz, H-5a″) and 3.54(dd, $J = 4.5$, 11.0 Hz, H-5b″) corresponding to an arabinopyrano pattern. The linkage position of the sugar moiety was considered to be through the C-3′ position due to the correlation between the anomeric proton $\delta$ 5.23(d, H-1″) and $\delta$ 148.50(s, C-3′) observed in the HMBC spectrum as well as the H-2′ of **9** shifted downfield by about 0.4 ppm in comparison with that with quercetin [14]. According to the evidence of the above spectral analysis, compound **9** was identified as quercetin-3′-*O*-β-arabinopyranoside. Compound **9** differed from crataeside (crataegoside) [15] in the sugar moiety where **9** was in the pyranoside form while crataeside was in the furanoside form. Thus, **9** was considered to be an isomer of craeside, and this was the first time that the $^{1}$H and $^{13}$C NMR data of **9** had been completely reported (Fig. 3).

Protein-tyrosine kinases (PTKs) are involved in signal transduction for cell growth and transformation [16–18] and thus become potential targets for controlling the growth of

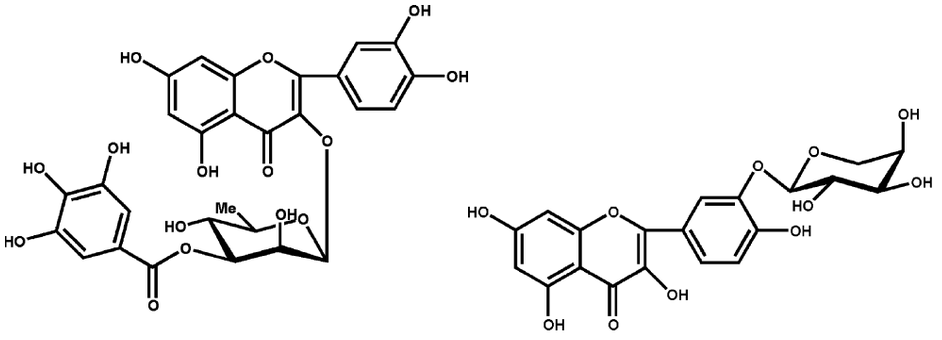



FIGURE 3 Chemical structures of compounds **4** and **9**.



transformed cells. The PTK bioassay directed fractionation of the ethanol extracts of the leaves led to the discovery that the cytotoxic activity was concentrated in the EtOAc fraction (PTK, $IC_{50}$ 540 μg/ml) and the *n*-BuOH fraction (PTK, $IC_{50}$ 650 μg/ml). Further bioassay for pure compounds led us to test that compounds **4** and **9** possessed PTK inhibition with $IC_{50}$ 24 μg/ml and $IC_{50}$ 40 μg/ml, respectively.

## EXPERIMENTAL SECTION

### General Experiment Procedures

Melting points were measured with a XT4A micromelting point apparatus and were uncorrected. EI and FABMS as well as MS/MS ESIMS and HPLC-ESIMS spectra were recorded on Finnigan TSQ 7000, ZAB-HS, and QSTAR-MS spectrometers; 1D and 2D NMR spectra were recorded on Bruker avance-500 MHz and Varian-300 MHz spectrometers with TMS as an internal standard and DMSO-$d_6$ as the solvent; IR spectra were measured on a Perkin–Elmer-559B Spectrophotometer (KBr disc); UV spectra were measured on Shimadzu UV-160A (MeOH). The silica gel and C-18 Lobar column were purchased from Qingdao Marine Chem. Factory and Sigma Co. The organic solvents and reagents were purchased from Beijing Chem. Corp.

### Plant Material

The leaves of *K. paniculata* Laxm (Sapindaceae) were collected in Badaling mountain area close to Beijing suburbs, China, in August 1998. The species was identified by Prof. Hubiao Chen, School of Pharmaceutical Sciences, Peking University, and a voucher specimen has been deposited in the Herbarium of the National Research Laboratory of Natural and Biomimetic Drugs, Peking University.

### Extraction and Isolation

The fresh leaves of *K. paniculata* (5.0 kg) were ground and extracted with 95% ethanol at room temperature. The extracts were concentrated under vacuum evaporation to afford

400 g residue, and the residue was partitioned between EtOAc and $H_2O$ and then between n-BuOH and $H_2O$. The EtOAc fractions were subjected to vacuum column chromatography on silica gel and eluted with $CHCl_3$–MeOH of increasing polarity from 20:1 to 1:1 to give 12 fractions. Fraction FE-3 (6.0 g) was chromatographed on silica gel using $CHCl_3$:MeOH (10:1) to yield compounds **5** (37 mg), **11** (16 mg) and **12** (45 mg); and $CHCl_3$:MeOH (5:1) to yield compounds **7** (12 mg), **1** (5.6 mg), **3** (4.2 mg), **15** (3.7 mg) and **16** (4.8 mg); fraction FE-5 (1.2 g) was subjected to sephadex LH-20 by eluting with MeOH:$H_2O$ (5:1) to afford compounds **2** (13.9 mg), **6** (7.8 mg), **13** (4.5 mg) and **14** (3.7 mg); and the *n*-BuOH fraction was subjected to repeated semi-preparative ODS HPLC by the mobile phase MeOH:$H_2O$ (1:5) to yield compounds **4** (5.8 mg), **8** (7.4 mg), **9** (3.6 mg) and **10** (11.2 mg).

Ethyl *p*-trigallate **1**, white amorphous powder. $C_{23}H_{18}O_{13}$, positive reaction showed dark blue color by $FeCl_3$· IR(KBr) $\nu_{max}$ 3270(br), 3215, 1703, 1610, 1400, 1200, 1155, 960, 870, 756. PFABMS *m/z* 525 [M + Na], 503 [M + 1], 471, 457, 305, 223, 185, 153, 137, 115, 93, 75. $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 1.25(t, $J = 6.9$ Hz, 3H); 4.17(q, $J = 6.9$ Hz, 2H), 6.90(s, 4H, H-2″, 6″, 2′, 6′), 6.92(s, 2H, H-2,6). $^{13}$C NMR data, see Table I.

3″-*O*-Galloyl-4′-*O*-galloyl-4-*O*-gallic-galloyl acid **2**, $C_{28}H_{18}O_{17}$, white amorphous powder. IR(KBr) $\nu_{max}$ cm$^{-1}$: 3360(br),3315, 1710, 1616, 1252, 1156, 988, 876, 750. $^1$H NMR $\delta$ppm: 6.99(s, 2H), 7.04(s, 2H), 7.04(s, 2H), 7.30(d, $J = 2.0$ Hz) and 7.09 (d, $J = 2.0$ Hz). $^{13}$C NMR data, see Table I. Positive FABMS *m/z*: 627 [M + 1], 665 [M + K], 457, 385, 339, 235, 305, 281, 265, 153. $^{13}$C NMR data were assigned in Table I.

*Ethylation*: Compound **2** (5 mg) and Dowex 50H$^+$ were stirred in 10 ml dry ethanol at room temperature under argon for 40 h [18]. The mixture, which contained an ethylated product as a major component in TLC, was filtered and concentrated, then 5 ml acetone and 1 ml 1N LiOH were added [19], and stirring was continued at room temperature for 4 h and monitored by TLC. The reacted mixture was diluted with 10 ml $CHCl_3$ and acidified to pH = 4 with 1 N HCl. Direct comparison of the components in $CHCl_3$ layer with **1** at silica gel TLC layer (mobile phase: $CHCl_3$/MeOH = 5 : 1) indicated that one of the hydrolysis products corresponded to compound **1** which was also checked by HPLC-ESI-MS spectrum. The evidence led us to propose a terminal gallic acid connected to the *meta* position of the third galloyl residue.

Ethyl *p*-heptagallate **3**, brown powder, dark blue color reaction with $FeCl_3$ reagent. RI(KBr) cm$^{-1}$: 3272, 1728, 1600, 1524, 1442, 1317, 1194, 1084, 1025, 982, 873, 826, 764. FAB-MS(*m/z*): 1149 (M$^+$ + K), 1111 (M + 1), 373, 199, 185, 153, MS/MS ESIMS *m/z*: 153, 197, 305, 457, 609, 761, 913, 1065, 1111 (M + 1). $^1$H NMR(DMSO-d6) $\delta$ 1.27(t, $J = 7.2$, 3H); 4.24(q, $J = 7.2$, 2H); $\delta$ 6.90(br, 14H). $^{13}$C NMR data were assigned in Table I.

3″-Galloylquercitrin **4**, yellow amorphous powder, appeared pale yellow at 254 nm and purple at 366 nm and yellow under UV/$NH_3$ on a TLC plate. IR(KBr) $\nu_{max}$ cm$^{-1}$: 3710, 1755, 1705, 1620, 1606, 1499, 1444, 1356,1307,1199,1166,1087,1033, 1007, 994, 959, 872, 813, 785, 764, 713. $^1$H NMR $\delta$ppm: 12.62(br, OH-5), 6.120(d, $J = 2.0$ Hz, H-6), 6.39 (d, $J = 2.0$ Hz, H-8), 7.32(dd, $J = 8.1$, 2.2 Hz, H-6′), 7.29(d, $J = 2.2$ Hz, H-2′), 7.03(s, 2H, H-2‴,6‴), 6.87(d, $J = 8.1$ Hz, H-5′), $\delta$ 5.20(br, H-1″), 4.26(br, H-2″), 5.00(dd, $J = 3.3$, 9.3 Hz, H-3″), 3.44(dd, $J = 9.3$, 8.5 Hz, H-4″), 3.32(m, H-5″), 0.88(d, $J = 6.0$ Hz, H-6″). FABMS *m/z*: 623 (M + Na), 601 (M + 1), 584, 564, 551, 525, 467, 444, 303, 229, 278, 185, 153, 115, 93, 75.

Quercetin-3′-*O*-β-D-arabinopyranoside **9**, yellow amorphous powder, and appeared pale yellow at 254 nm and purple at 366 nm and yellow under UV/$NH_3$ on a TLC plate. IR(KBr) $\nu_{max}$ cm$^{-1}$: 3542, 3215, 1710, 1701, 1624, 1592, 1200, 1150, 976, 897, 820, 750.

TABLE II $^{13}$C NMR data of compounds **4**, **5**, **7** and **9**

| C | 4 | 5 | 6 | 7 | 9 |
|---|---|---|---|---|---|
| 2 | 156.55,s | 77.94,d | 76.81,d | 156.72,s | 146.40,s |
| 3 | 134.53,s | 64.81,d | 66.50,d | 133.44,s | 135.72,s |
| 4 | 177.86,s | 28.08,t | 27.10,t | 177.34,s | 176.21,s |
| 5 | 161.35,s | 155.63,s | 155.32,s | 160.93,s | 156.22,s |
| 6 | 98.82,d | 94.98,d | 94.34,d | 98.07,d | 98.32,d |
| 7 | 164.38,s | 156.11,s | 155.80,s | 164.27,s | 164.18,s |
| 8 | 93.75,d | 94.00,d | 93.82,d | 92.80,d | 93.61,d |
| 9 | 157.36,s | 156.50,s | 156.52,s | 156.74,s | 160.11,s |
| 10 | 104.41,s | 98.37,s | 98.35,s | 103.39,s | 104.56,s |
| 1′ | 120.74,s | 130.48,s | 130.89,s | 120.46,s | 122.23,s |
| 2′ | 115.54,d | 114.65,d | 115.00,d | 130.16,d | 115.61,d |
| 3′ | 145.38,s | 144.37,s | 145.34,s | 114.19,d | 148.50,s |
| 4′ | 148.60,s | 144.37,s | 146.22,s | 160.49,s | 146.48,s |
| 5′ | 115.53,d | 114.78,d | 114.42,d | 114.19,d | 115.92,d |
| 6′ | 120.74,d | 117.85,d | 118.10,d | 130.16,d | 120.12,d |
| 1″ | 102.17,d | | | 102.47,d | 103.45,d |
| 2″ | 67.81,d | | | 70.70,d | 69.69,d |
| 3″ | 73.82,d | | | 71.98,d | 70.87,d |
| 4″ | 68.50,d | | | 66.98,d | 67.10,d |
| 5″ | 71.00,d | | | 64.85,t | 65.25,t |
| 6″ | 17.54,q | | | | |
| CO‴ | 165.82,s | | 165.23,s | | |
| 1‴ | 120.02,s | | 121.23,s | | |
| 2⁗,6‴ | 109.04,s | | 108.78,d | | |
| 3‴,5‴ | 145.47,s | | 145.44,s | | |
| 4‴ | 138.36,s | | 138.20,s | | |

$^1$H NMR(DMSO-d6, 500 MHz): $\delta$ 6.27(d, $J = 3.5$ Hz, H-6), 6.46(d, $J = 3.5$ Hz, H-8), 7.67(dd, $J = 8.5$, 2.0 Hz, H-6′), 7.84(d, $J = 2.0$ Hz, H-2′), 6.96(d, $J = 8.5$ Hz, H-5′), 5.23 (d, $J = 6.5$ Hz, H-1″), 3.99(dd, $J = 6.5$, 8.5 Hz, H-2″), 3.73(dd, $J = 3.0$, 8.5 Hz, H-3″), 3.90(ddd, $J = 3.0$, 4.0, 4.5 Hz, H-4″), 3.92(dd, $J = 4.0$, 11.0 Hz, H-5a″), 3.54(dd, $J = 4.5$, 11.0 Hz, H-5b″). $^{13}$C NMR data were assigned in Table II.

### *Acknowledgements*

The authors are grateful for the grant supported by NNSF of China (No. 29732040). Thanks are also due to Mr Lu Shan of Analytical and Testing Center, Beijing Normal University for NMR spectral measurements.

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