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CHLOROGENIC ACIDS FROM GREEN COFFEE BEANS COLLECTED IN TAY NGUYEN PROVINCES OF VIET NAM

Do Thi Thanh Huyen[1], Ngo Thi Phuong[1], Cao Son Tung[2], Le Ngoc Hung[3], Phuong Anh Tuan[1], Nguyen Tuan Anh[2], Le Minh Ha[1,*]

[1]*Institute of Natural Products Chemistry, Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Cau Giay, Ha Noi, Viet Nam*

[2]*University of Science and Technology, 1 Dai Co Viet, Ha Noi, Viet Nam*

[3]*Pharmaceutical Chemistry Lab Project, Center for Research and Technology Transfer, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi, Viet Nam*

[*]Email: *halm2vn@gmail.com*

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Abstract. Six chlorogenic acid compounds, including 5-*O*-caffeoyquinic acid (**1**), 3-*O*-caffeoyquinic acid (**2**), 4-*O*-caffeoyquinic acid (**3**), 3,5-*O*-dicaffeoylquinic acid (**4**), 3,4-*O*-dicaffeoylquinic acid (**5**) and 4,5-*O*-dicaffeoylquinic acid (**6**) were isolated from the methanol extract of green coffee beans collected in Gia Lai and Kon Tum (Tay Nguyen provinces) of Viet Nam. Their structures were determined by ESI-MS, 1D and 2D NMR spectra and by comparison with the reported spectral data. This is the first report on the isolation of chlorogenic acid compounds from green coffee beans of Viet Nam. 3-*O*-caffeoyquinic acid was isolated as the main component with extraction efficiency of 0.58 % compared to dried material weight.

Keywords: green coffee beans, *Coffea arabica*, chlorogenic acid, 3-*O*-caffeoyquinic acid.

Classification numbers: 1.1.1.

1. INTRODUCTION

Coffee, belonging to Rubiaceae family, is one of the most consumed beverages worldwide which is prepared by the ripe seeds from the coffee plants. Chemical investigations showed that coffee is rich in bioactive compounds, such as chlorogenic acids, phenolic compounds, caffeine, trigonelline, diterpenes, and melanoidins [1]. Green coffee is a form of raw, unroasted, unprocessed and natural coffee fruits [2]. As a functional food with antioxidant properties, coffee reduces the incidence of cancer, diabetes and liver diseases, protects against Parkinson's disease and reduces mortality risk. Chlorogenic acids (CGAs) are phenolic compounds formed by the esterification of cinnamic acids, such as caffeic, ferulic, and p-coumaric acids, with (-)-quinic acid. A series of health benefits have been associated with the consumption of CGAs in the last few years, such as reduction of the relative risk of cardiovascular disease, diabetes type 2, Alzheimer's disease, antibacterial and antiinflammatory activities. Green coffee is a major source of CGAs in nature. Recent studies demonstrated that the consumption of green coffee extracts produced antihypertensive effect in rats and humans, improvement in human

vasoreactivity, inhibitory effect on fat accumulation and body weight in mice and humans, and modulation of glucose metabolism in humans [3]. Viet Nam is the 2nd largest coffee exporting country in the world with an abundant resource of organic green coffee beans (the Central Highlands provinces are very famous for growing coffee in Viet Nam). However, there has not been any research on the chemical composition of coffee beans of Viet Nam. Therefore, in this paper, we report the results of isolation and structural determination of six chlorogenic acid compounds from green coffee beans (*Coffea arabica*) collected in Tay Nguyen provinces of Viet Nam.

2. EXPERIMENTAL

2.1. Plant materials

The green seeds of *Coffea arabica* were collected in Gia Lai, Kon Tum, Tay Nguyen provinces, Viet Nam in February 2020. The scientific name was identified by Dr. Nguyen Van Du, Institute of Ecology and Biological Resources, Vietnam Academy of Science and Technology (VAST). The voucher specimens (CF-02.2020) were deposited in Institute of Natural Products Chemistry, VAST.

2.2. General experimental procedures

The ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectra were recorded on a Bruker AM500 FT-NMR spectrometer. ESI-MS spectra were obtained from an Agilent 1100 Series LC/MSD Trap SL. Column chromatography (CC) was performed on silica gel (0.040 - 0.063 mm) and YMC RP-18 resins (30 - 50 μm). Thin layer chromatography (TLC) was conducted on pre-coated silica gel 60 F_{254} and RP-18 F_{254S} plates. Compounds were visualized by UV light at 254 and 365 nm, and by spraying with the solution of 10 % H_2SO_4 in ethanol, followed by heating.

2.3. Extraction and isolation

The powder of dried green coffee beans (2.0 kg) was extracted in turn with n-hexane, ethyl acetate, and methanol to give n-hexane (10.5 g), EtOAc (22.0 g), methanol (35.0 g) extracts, respectively. The methanol extract was fractionated by a silica gel column using the gradient of EtOAc-methanol (10:1, 5:1, 1:1, 1:2, 0:100, v:v) to obtain 5 fractions (M1→M5). The fraction M2 (6.5 g) was chromatographed on a silica gel column with a solvent mixture of EtOAc-methanol-water (7:1:0.5) to obtain four sub-fractions (M2.1 to M2.4). The sub-fraction M2.2 (1.6 g) was then recrystallized in the mixture of chloroform-methanol (1:1) to obtain compound **1** (15.0 mg). Purification of the sub-fraction M2.3 (1.3 g) by a silica gel column using EtOAc-methanol-water (5:1:0.5) gave compound **3** (18.0 mg). The fraction M3 (5.8 g) was first subjected to a silica gel column eluted with chloroform-methanol-water (5:1:0.3) then separated by a silica gel column using chloroform-methanol-water (5:1:0.5) as eluent to afford compound **2** (115.5 mg). The fraction M4 (6.2 g) was passed through a silica gel column and eluted with to obtain three sub-fractions (M4.1 to M4.3). The sub-fractions M4.1 (2.5 g) was further separated on a silica gel column eluting with chloroform-methanol-water (8:1:1) to achieve three smaller sub-fractions (M4.1.1 to M4.1.3). Compound **4** (12.5 mg) was obtained from the sub-fraction M4.1.1 by using YMC RP-18 column with methanol-water (2:1). The sub-fraction M4.1.2 was purified on a YMC RP-18 column eluting with methanol-water (3:1) to afford compound **5** (10.5

mg). The fraction M5 (4.5 g) was separated on a silica gel column with a solvent mixture of EtOAc-methanol-water (4:1:0.4) to provide four sub-fractions (M5.1 to M5.4). Compound **6** was obtained by recrystallizing the sub-fraction M5.2 in the mixture of chloroform-methanol (1:1).

5-*O*-caffeoyl quinic acid (1): white powder. ESI-MS *m/z*: 355.1 $[M+H]^+$ ($C_{16}H_{18}O_9$). ^{1}H-NMR (500 MHz, CD_3OD), δ (ppm): 2.05 (1H, m, H-6ax), 2.10 (1H, m, H-2ax), 2.20 (1H, dd, *J* = 14.0, 3.0 Hz H-2eq), 2.25 (1H, dm, H-6eq), 3.74 (1H, dd, *J* = 8.5, 3.0 Hz, H-4ax), 4.19 (1H, m, H-3eq), 5.35 (1H, m, H-5ax), 6.27 (1H, d, *J* = 16.0 Hz, H-8′), 6.80 (1H, d, *J* = 8.5 Hz, H-5′), 6.97 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 7.07 (1H, d, *J* = 2.0 Hz, H-2′), 7.56 (1H, d, *J* = 16.0 Hz, H-7′). ^{13}C-NMR (125 MHz, CD_3OD), see Table 1.

3-*O*-caffeoyl quinic acid (2): white powder. ESI-MS *m/z*: 355.2 $[M+H]^+$ ($C_{16}H_{18}O_9$). ^{1}H-NMR (500 MHz, CD_3OD), δ (ppm): 1.98 (1H, dd, *J* = 13.5, 9.5 Hz, H-6ax), 2.15 (2H, m, H-2ax, H-6eq), 2.23 (1H, dd, *J* = 14.5, 3.5 Hz H-2eq), 3.66 (1H, dd, *J* = 8.5, 3.5 Hz, H-4ax), 4.17 (1H, m, H-5ax), 5.37 (1H, m, H-3eq), 6.33 (1H, d, *J* = 16.0 Hz, H-8′), 6.79 (1H, d, *J* = 8.0 Hz, H-5′), 6.96 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 7.06 (1H, d, *J* = 2.0 Hz, H-2′), 7.60 (1H, d, *J* = 15.5 Hz, H-7′). ^{13}C-NMR (125 MHz, CD_3OD), see Table 1.

4-*O*-caffeoyl quinic acid (3): white powder. ESI-MS *m/z*: 355.1 $[M+H]^+$ ($C_{16}H_{18}O_9$). ^{1}H-NMR (500 MHz, CD_3OD), δ (ppm): 2.07 (1H, brs, H-6ax), 2.09 (1H, brs, H-2ax), 2.20 (1H, brs, H-2eq), 2.23 (1H, brs, H-6eq), 4.29 (1H, brd, *J* = 4.5 Hz, H-5ax), 4.38 (1H, brs, H-3eq), 4.56 (1H, brs, H-4ax), 6.38 (1H, d, *J* = 15.5 Hz, H-8′), 6.78 (1H, d, *J* = 8.5 Hz, H-5′), 6.96 (1H, d, *J* = 8.0 Hz, H-6′), 7.07 (1H, d, *J* = 1.5 Hz, H-2′), 7.60 (1H, d, *J* = 15.5 Hz, H-7′). ^{13}C-NMR (125 MHz, CD_3OD), see Table 1.

3,5-*O*-dicaffeoyl quinic acid (4): pale yellow powder. ESI-MS *m/z*: 517.2 $[M+H]^+$ ($C_{25}H_{24}O_{12}$). ^{1}H-NMR (500 MHz, CD_3OD), δ (ppm): 2.18 (1H, dd, *J* = 14.0, 7.0 Hz, H-6ax), 2.24 (2H, brs, H-2), 2.35 (1H, dd, *J* = 14.0, 4.0 Hz, H-6eq), 3.99 (1H, dd, *J* = 7.5, 3.5 Hz, H-4ax), 5.41 (1H, m, H-3eq), 5.45 (1H, m, H-5ax), 6.29 (1H, d, *J* = 16.0 Hz, H-8′/H-8″), 6.36 (1H, d, *J* = 16.0 Hz, H-8′/H-8″), 6.80 (2H, d, *J* = 8.5 Hz, H-5′/H-5″), 6.98 (2H, dd, *J* = 6.5, 2.0 Hz, H-6′/H-6″), 7.08 (2H, d, *J* = 2.0 Hz, H-2′/H-2″), 7.60 (1H, d, *J* = 16.0 Hz, H-7′/H-7″), 7.63 (1H, d, *J* = 16.0 Hz, H-7′/H-7″). ^{13}C-NMR (125 MHz, CD_3OD), see Table 1.

3,4-*O*-dicaffeoyl quinic acid (5): pale yellow powder. ESI-MS *m/z*: 517.1 $[M+H]^+$ ($C_{25}H_{24}O_{12}$). ^{1}H-NMR (500 MHz, CD_3OD), δ (ppm): 2.10 (1H, dd, *J* = 13.5, 10.0 Hz, H-2ax), 2.15 (1H, m, ddd, *J* = 15.0, 4.5, 2.5 Hz, H-6ax), 2.24 (1H, ddd, *J* = 13.5, 4.0, 2.5 Hz, H-6eq), 2.37 (1H, dd, *J* = 15.0, 3.5 Hz, H-2eq), 4.39 (1H, m, H-5ax), 5.00 (1H, dd, *J* = 9.0, 3.5 Hz, H-4ax), 5.65 (1H, m, H-3eq), 6.27 (1H, d, *J* = 16.0 Hz, H-8′/H-8″), 6.30 (1H, d, *J* = 16.0 Hz, H-8′/H-8″), 6.75 (2H, d, *J* = 8.0 Hz, H-5′/H-5″), 6.79 (2H, d, *J* = 8.5 Hz, H-5′/H-5″), 6.89 (2H, dd, *J* = 8.5, 2.0 Hz, H-6′/H-6″), 6.95 (2H, dd, *J* = 8.5, 2.0 Hz, H-6′/H-6″), 7.04 (2H, d, *J* = 2.0 Hz, H-2′/H-2″), 7.06 (2H, d, *J* = 2.0 Hz, H-2′/H-2″), 7.56 (1H, d, *J* = 16.0 Hz, H-7′/H-7″), 7.60 (1H, d, *J* = 16.0 Hz, H-7′/H-7″). ^{13}C-NMR (125 MHz, CD_3OD), see Table 1.

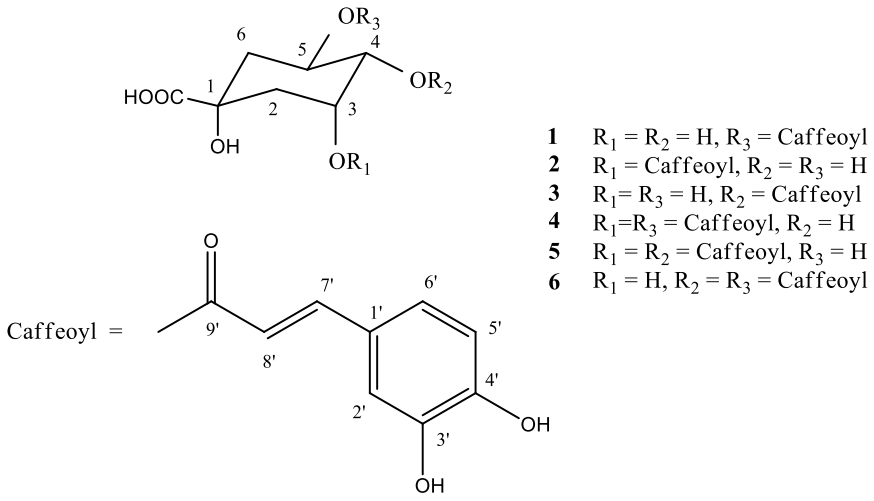
4,5-*O*-dicaffeoyl quinic acid (6): pale yellow powder. ESI-MS *m/z*: 517.1 $[M+H]^+$ ($C_{25}H_{24}O_{12}$). ^{1}H-NMR (500 MHz, CD_3OD), δ (ppm): 2.14 (1H, m, H-2ax), 2.24 (1H, m, H-2eq), 2.30 (2H, m, H-6), 4.39 (1H, m, H-3eq), 5.13 (1H, dd, J = 9.0, 3.0 Hz, H-4ax), 5.64 (1H, m, H-5ax), 6.20 (1H, d, *J* = 16.0 Hz, H-8′/H-8″), 6.30 (1H, d, *J* = 16.0 Hz, H-8′/H-8″), 6.76 (1H, d, *J* = 8.0 Hz, H-5′/H-5″), 6.77 (1H, d, *J* = 8.0 Hz, H-5′/H-5″), 6.89 (2H, dd, *J* = 8.5, 2.0 Hz, H-6′/H-6″), 6.93 (2H, dd, *J* = 8.5, 2.0 Hz, H-6′/H-6″), 7.02 (2H, d, *J* = 2.0 Hz, H-2′/H-2″), 7.04 (2H, d, *J* = 2.0 Hz, H-2′/H-2″), 7.54 (1H, d, *J* = 16.0 Hz, H-7′/H-7″), 7.61 (1H, d, *J* = 16.0 Hz, H-7′/H-7″). ^{13}C-NMR (125 MHz, CD_3OD), see Table 1.

3. RESULTS AND DISCUSSION

Compound **1** was obtained as a white powder and showed the pseudo molecular ion peak $[M+H]^+$ at *m/z* = 355.1 in the positive ESI-MS, corresponding to $C_{16}H_{18}O_9$. The ^{1}H- and ^{13}C-NMR spectra of **1** showed the signals of a caffeoyl group. In the aromatic region, resonances for the ABX system [δ_H 7.07 (1H, d, *J* = 2.0 Hz), 6.80 (1H, d, *J* = 8.5 Hz), and 6.97 (1H, dd, *J* = 8.5, 2.0 Hz)] were observed, which were assigned to 1,3,4-trisubstituted phenyl unit. Two olefin protons [δ_H 6.27 (1H, d, *J* = 16.0 Hz) and 7.56 (1H, d, *J* = 16.0 Hz)] with coupling constant of 16.0 Hz suggested *trans* caffeoyl group. The presence of quinic acid unit was inferred from ^{1}H-NMR of **1** with three oxymethine protons [δ_H 3.74 (1H, dd, *J* = 8.5, 3.0 Hz, H-4), 4.19 (1H, m, H-3), 5.35 (1H, m, H-5)] and two sp^3 methylenes [δ_H 2.05 (1H, m, H-6ax), 2.10 (1H, m, H-2ax), 2.20 (1H, dd, *J* = 14.0, 3.0 Hz H-2eq), 2.25 (1H, dm, H-6eq)]. The assignments were determined by analysis of ^{13}C-NMR, HSQC, ^{1}H-^{1}H COSY spectra. Once the oxygenated methine of quinic acid was acylated by caffeoyl, the proton signal will shift downfield [4]. The deshielded resonance of H-5 (δ_H 5.35) suggested acylation of the hydroxy group at C-5. The position of caffeoyl group at C-5 was further confirmed by HMBC cross-peak between H-5 (δ_H 5.35) and C-9′ (δ_C 168.68). Based on the spectroscopic evidence, the structure of compound **1** was identified as 5-*O*-caffeoyl quinic acid by comparison with the published data [5].

Compound **2** was also obtained as a white powder and showed the pseudo molecular ion peak $[M+H]^+$ at *m/z* = 355.1 in the positive ESI-MS, corresponding to $C_{16}H_{18}O_9$. The NMR spectra of **2** showed characteristic signals very similar to those of **1**. The ^{1}H-NMR spectra revealed a quinic acid unit [δ_H 1.98 (1H, dd, *J* = 13.5, 9.5 Hz, H-6ax), 2.15 (2H, m, H-2ax, H-6eq), 2.23 (1H, dd, *J* = 14.5, 3.5 Hz H-2eq), 3.66 (1H, dd, *J* = 8.5, 3.5 Hz, H-4), 4.17 (1H, m, H-5), 5.37 (1H, m, H-3)] and a caffeoyl group [δ_H 6.33 (1H, d, *J* = 16.0 Hz, H-8′), 6.79 (1H, d, *J* = 8.0 Hz, H-5′), 6.96 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′), 7.06 (1H, d, *J* = 2.0 Hz, H-2′), 7.60 (1H, d, *J* = 15.5 Hz, H-7′)]. The coupling constant $J_{H\text{-}7',H\text{-}8'}$ of 16.0 Hz indicated a *trans* configuration of the caffeoyl group. The only difference between two compounds revealed by the chemical shifts of H-3 and H-5. In the ^{1}H-NMR spectrum of **2**, the downfield shift of the resonance of H-3 (δ_H 5.37) suggested that the hydroxy group on C-3 was acylated with a caffeic acid [6]. The prediction was confirmed by HMBC correlation from H-3 (δ_H 5.37) to C-9′ (δ_C 168.68). The ^{1}H- and ^{13}C-NMR data of **2** were identical to those of 3-*O*-caffeoyl quinic acid reported [6]. Therefore, compound **2** was identified as 3-*O*-caffeoyl quinic acid, which was isolated as the main component with extraction efficiency of 0.58 % compared to dried material weight.

Compound **3** was obtained as a white powder. Similar to compounds **1** and **2**, the molecular formula of **3** was deduced as $C_{16}H_{18}O_9$ based on pseudo molecular ion peak $[M+H]^+$ at *m/z* = 355.2 obtained from the ESI-MS spectrum. The presence of a caffeoyl group and a quinic acid moiety were inferred from the resonance signals on ^{1}H- and ^{13}C-NMR spectra of **3**. The ^{13}C-NMR data revealed the presence of a quinic acid moiety characterized with two methylenes (δ_C 39.0 and 42.5), three oxymethines [δ_C 66.2 (C-5), 68.8 (C-3), 79.3 (C-4)], a quaternary carbon (δ_C 77.1), and a carboxyl group (δ_C 177.3). The ^{1}H-NMR data displayed three oxymethine protons [4.29 (1H, brd, *J* = 4.5 Hz, H-5), 4.38 (1H, brs, H-3), 4.56 (1H, brs, H-4)] and two sp3 methylenes [2.07 (1H, brs, H-6ax), 2.09 (1H, brs, H-2ax), 2.20 (1H, brs, H-2eq), 2.23 (1H, brs, H-6eq)] typical of a quinic acid moiety. The HSQC, ^{1}H-^{1}H COSY spectra were used to confirm the predicted structure. The downfield shifts of H-4 (δ_H 4.56) and C-4 (δ_C 79.3) suggested esterification of the hydroxy group at C-4 [6]. T*rans* configuration of the caffeoyl group was identified based on the coupling constant $J_{H\text{-}7',H\text{-}8'}$ of 16.0 Hz. According to the spectral analysis and comparison with the published data [6-8], compound **3** was determined to be 4-*O*-caffeoyl quinic acid.



1 $R_1 = R_2 = H$, R_3 = Caffeoyl
2 R_1 = Caffeoyl, $R_2 = R_3 = H$
3 $R_1 = R_3 = H$, R_2 = Caffeoyl
4 $R_1 = R_3$ = Caffeoyl, $R_2 = H$
5 $R_1 = R_2$ = Caffeoyl, $R_3 = H$
6 $R_1 = H$, $R_2 = R_3$ = Caffeoyl

Figure 1. Chemical structures of chlorogenic acids isolated from green coffee beans (**1**-**6**).

Compound **4** was obtained as a pale yellow powder. The molecular formula of **4** was clarified as $C_{25}H_{24}O_{12}$ based on the ion at *m/z* = 517.2 $[M+H]^+$ in the ESI-MS spectrum. The ^{1}H- and ^{13}C-NMR spectra of **4** showed the characteristic signals of a quinic acid moiety including three oxymethines [δ_H 3.99 (1H, dd, *J* = 7.5, 3.5 Hz, H-4), 5.41 (1H, m, H-3), 5.45 (1H, m, H-5) / δ_C 72.1 (C-4), 72.7 (C-3), 73.0 (C-5)], two methylenes [δ_H 2.18 (1H, dd, *J* = 14.0, 7.0 Hz, H-6), 2.24 (2H, brs, H-2), 2.35 (1H, dd, *J* = 14.0, 4.0 Hz, H-6) / δ_C 36.1 (C-6), 38.3 (C-2)], and a carboxyl group (δ_C 178.0). In the aromatic region, resonance signals for two ABX systems [6.80 (2H, d, *J* = 8.5 Hz, H-5′/H-5″), 6.98 (2H, dd, *J* = 6.5, 2.0 Hz, H-6′/H-6″), 7.08 (2H, d, *J* = 2.0 Hz, H-2′/H-2″)] were observed, which were assigned to two 1,3,4-trisubstituted phenyl units. Two pairs of doublets with coupling constants of 16.0 Hz indicative of *trans* olefinic protons suggested the presence of two *trans* caffeoyl groups. The HSQC, ^{1}H-^{1}H COSY spectra were supported for NMR data assignment of **4**. The position of the two *trans* caffeoyl groups on quinic acid was established by the downfield shift of the proton signals at δ_H 5.41 (H-3), δ_H 5.43 (H-5) and HMBC correlations from H-3, H-5 to two ester carbon at δ_C 168.4, 168.9. Therefore, the structure of **4** was determined to be 3,5-*O*-dicaffeoyl quinic acid by comparison with the reported literature [9].

Compound **5** was obtained as a pale yellow powder with a molecular formula was $C_{25}H_{24}O_{12}$, determined by the ion at *m/z* = 517.1 $[M+H]^+$ in the ESI-MS spectrum. The ^{1}H- and ^{13}C-NMR spectra of **5** were similar to those of **4** except for the downfield shifts of H-3 (δ_H 5.65) and H-4 (δ_H 5.00), suggesting the difference in the substituted positions of two *trans* caffeoyl groups on quinic acid. The assignment was completely based on the data obtained from the HSQC and ^{1}H-^{1}H COSY spectra. Besides, the long range correlations between H-3 (δ_H 5.65) and H-4 (δ_H 5.00) and two ester carbon at δ_C 168.6 which were observed from HMBC spectra of **5** indicated that the esterification of the hydroxy groups at C-3 and C-4. From the detailed analysis of NMR, ESI-MS spectra and comparison with reported data [10], compound **5** was determined as 3,4-*O*-dicaffeoyl quinic acid.

Compound **6** was also obtained as a pale yellow powder. The ESI-MS spectrum of compound **6** showed the pseudo molecular ion at m/z = 517.1 $[M+H]^+$, indicating the molecular formula $C_{25}H_{24}O_{12}$. Similar to compounds **4** and **5**, compound **6** was also predicted as a dicaffeoyl quinic acid based on the resonances obtained from NMR spectra. Two ABX systems

[6.76 (1H, d, *J* = 8.0 Hz, H-5′/H-5″), 6.77 (1H, d, *J* = 8.0 Hz, H-5′/H-5″), 6.89 (2H, dd, *J* = 8.5, 2.0 Hz, H-6′/H-6″), 6.93 (2H, dd, *J* = 8.5, 2.0 Hz, H-6′/H-6″), 7.02 (2H, d, *J* = 2.0 Hz, H-2′/H-2″), 7.04 (2H, d, *J* = 2.0 Hz, H-2′/H-2″)] and two pairs of olefinic protons with coupling constants of 16.0 Hz suggested the presence of two *trans* caffeoyl groups. The position of caffeoyl groups on quinic acid was proved by the deshielded resonances of H-4 (δ_H 5.13), H-5 (δ_H 5.64) and the HMBC crosspeaks from H-4, H-5 to two ester carbon at δ_C 168.2, 168.6. From above evidence and comparison with literature [11-12], compound **6** was deduced to be 4,5-*O*-dicaffeoyl quinic acid.

Table 1. ^{13}C NMR data for compounds **1**-**6**.

C	**1**		**2**		**3**		**4**		**5**		**6**	
	δ_C	δ_C[a]	δ_C	δ_C[b]	δ_C	δ_C[c]	δ_C	δ_C[d]	δ_C	δ_C[e]	δ_C	δ_C[f]
1	76.1	76.2	75.4	75.4	77.1	76.6	74.8	75.2	76.6	76.5	76.1	75.8
2	38.2	38.1	36.7	36.7	39.0	38.4	38.3	38.4	37.0	36.9	38.4	38.5
3	71.3	71.4	73.0	73.0	68.8	69.6	72.7	72.2	70.2	72.1	69.0	68.6
4	73.5	73.6	74.8	74.8	79.3	79.3	72.1	71.2	75.2	75.1	75.8	75.7
5	72.0	71.9	68.3	68.3	66.2	65.5	73.0	73.0	65.8	65.7	69.4	69.8
6	38.8	38.9	41.5	41.5	42.5	42.7	36.1	36.4	42.0	41.9	39.4	39.7
7	177.0	177.0	178.4	178.3	177.3	177.3	178.0	176.4	178.0	177.9	176.8	176.4
1′	127.8	127.8	128.0	127.9	127.9	127.8	128.0	127.8	127.6	127.5	127.7	127.7
2′	115.3	115.3	115.2	115.1	115.3	115.1	115.2	115.1	115.3	115.2	115.2	115.2
3′	146.8	146.6	146.8	146.8	146.8	146.8	146.8	144.5	146.8	146.7	146.8	146.8
4′	149.5	149.4	149.4	149.4	149.5	149.6	149.6	149.6	149.6	149.5	149.7	149.8
5′	116.5	116.5	116.5	116.4	116.5	116.5	116.5	116.4	116.5	116.5	116.5	116.6
6′	123.0	123.0	122.9	122.9	123.0	123.0	123.1	122.9	123.1	122.0	123.1	123.3
7′	147.1	147.0	146.8	146.8	147.2	147.1	147.3	147.2	147.4	147.3	147.7	147.7
8′	115.2	115.3	115.9	115.8	115.4	115.4	115.3	115.2	115.0	114.9	114.7	114.7
9′	168.7	168.7	169.1	169.0	169.1	169.0	168.9	168.5	168.6	168.5	168.6	168.4
1″							127.8	127.9	127.8	127.6	127.7	127.8
2″							115.2	115.1	115.2	115.1	115.2	115.3
3″							146.8	144.5	146.8	146.7	146.8	146.9
4″							149.6	149.6	149.6	149.5	149.7	149.8
5″							116.5	116.4	116.5	116.4	116.5	116.6
6″							123.0	122.9	123.2	123.2	123.1	123.3
7″							147.3	147.0	147.3	147.3	147.6	147.8
8″							115.6	115.7	115.0	114.9	114.8	114.8
9″							168.4	169.0	168.6	168.6	168.2	168.7

[a] δ_C of 5-*O*-caffeoyl quinic acid [5]; [b] δ_C of 3-*O*-caffeoyl quinic acid [6]; [c] δ_C of 4-*O*-caffeoyl quinic acid [7]; [d] δ_C of 3,5-*O*-dicaffeoyl quinic acid [9]; [e] δ_C of 3,4-*O*-dicaffeoyl quinic acid [10]; [f] δ_C of 4,5-*O*-dicaffeoyl quinic acid [11].

4. CONCLUSION

From the methanol extract of green coffee beans (*Coffea arabica*) collected in Gia Lai and Kon Tum, Tay Nguyen provinces of Viet Nam, six chlorogenic acid compounds, including 5-caffeoyquinic acid (**1**), 3-caffeoyquinic acid (**2**), 4-caffeoyquinic acid (**3**), 3,5-dicaffeoylquinic acid (**4**), 3,4-dicaffeoylquinic acid (**5**) and 4,5-dicaffeoylquinic acid (**6**) were isolated and identified of their structures. All these compounds are first reported from green coffee bean collected in Viet Nam.

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