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Cimiracemates A–D, phenylpropanoid esters from the rhizomes of *Cimicifuga racemosa*

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Abstract

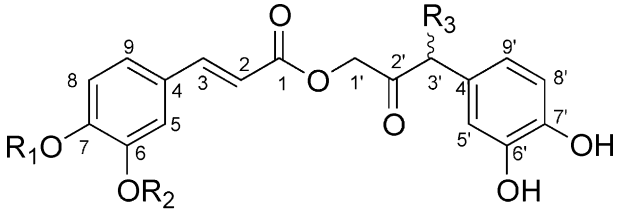
Four phenylpropanoid esters, cimiracemates A–D (**1–4**), along with three known compounds, isoferulic acid, ferulic acid and methyl caffeate were isolated from the EtOAc fraction of the rhizome of *Cimicifuga racemosa*. The structures of the esters were elucidated by means of spectral data, including 2D NMR spectroscopy.

Keywords: *Cimicifuga racemosa*; Ranunculaceae; Black cohosh; Chemical components; Phenylpropanoid esters; Cimiracemates A–D

1. Introduction

The roots and rhizomes of *Cimicifuga racemosa* (L.) Nutt. (*Actaea racemosa* L.) (Ranunculaceae) (Compton et al., 1998), commonly known as black cohosh, have a long and diverse history of medicinal use dating back to native North American indigenous groups (Foster, 1999; McKenna et al., 2001). It is presently used in the treatment of climacteric symptoms related to menopause (Liske, 1998; Lieberman, 1998), with a clinical history spanning over the last 40 years (Stielhler, 1959; Foeldes, 1959; Stefen, 1959; Brucker, 1960; Schildge, 1964; Stolze, 1982; Vorberg, 1984; Jarry and Harnischfeger, 1985; Jarry et al., 1985; Pethoe, 1987; Duker et al., 1991). As part of our studies on botanical dietary supplements for women's health, we have been investigating the biological and chemical profiles of the rhizomes of this plant. Previously, we reported on the isolation and structure elucidation of 26-deoxyactein and the clarification of the nomenclature of 27-deoxyactein (Chen et al., 2002b), as well as on the isolation and structure determination of eight new 9,19-cyclolanostane-triterpene glycosides (cimiracemosides I-P) (Chen et al., 2002a).

In the present investigation, four phenylpropanoid esters, cimiracemates A–D (**1–4**) were isolated along with three known compounds: isoferulic acid, ferulic acid, and methyl caffeate from the rhizomes of *C. racemosa*. In this paper, the isolation of these compounds and the elucidation of their structures by means of spectral data are described.



1. R_1= Me, R_2=H, R_3=H
2. R_1= H, R_2=Me, R_3=H
3. R_1= Me, R_2=H, R_3= OMe
4. R_1= H, R_2=Me, R_3= OMe

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2. Results and discussions

Cimiracemates A–D (**1–4**) were obtained by repeated chromatography of the EtOAc fraction prepared from the rhizomes of *C. racemosa* by sequential chromatography on silica gel (SiO_2) and RP-18 columns, and C-18 HPLC.

Cimiracemate A (**1**) was obtained as a light brown powder. The molecular formula was determined to be $C_{19}H_{18}O_7$ on the basis of a negative HR-ESIMS *m/z* 357.0974 (calc. 357.0974 for $C_{19}H_{17}O_7$). UV absorptions at 291 (log ε: 3.77) and 325 (log ε: 3.96) nm showed that **1** has a conjugated aromatic system. In the ^{1}H NMR spectrum, signals at δ_H 7.61 and 6.36 (each 1H, *d*, $J = 15.9$ Hz) indicated the presence of a *trans*-ethylene group conjugated with the aromatic ring. Two groups of typical ABX spin system signals for 1,2,4-trisubstituted aromatic ring protons were observed at δ_H 7.09 (1H, *d*, $J = 2.1$ Hz), 7.06 (1H, *dd*, $J = 2.1$, 8.3 Hz), and 6.94 (1H, *d*, $J = 8.3$ Hz); and δ_H 6.73 (1H, *d*, $J = 8.0$ Hz), 6.68 (1H, *d*, $J = 2.0$ Hz), and 6.57 (1H, *dd*, $J = 2.0$, 8.0 Hz). The spectrum also showed one methoxyl signal at δ_H 3.88 (3H, *s*), and two methylene signals at δ_H 3.63 (2H, *s*) and 4.86 (2H, *s*). The ^{13}C and DEPT NMR spectra of **1** showed signals ascribable to a *trans*-ethylene group at δ_C 115.2 (*d*, C-2) and 147.4 (*d*, C-3), as well as two signal groups for 1,2,4-trisubstituent aromatic ring at δ_C 128.8 (*s*, C-4), 114.8 (*d*, C-5), 148.0 (*s*, C-6), 151.7 (*s*, C-7), 112.5 (*d*, C-8), 123.0 (*d*, C-9); and δ_C 126.0 (*s*, C-4′), 117.6 (*d*, C-5′), 146.6 (*s*, C-6′), 145.7 (*s*, C-7′), 116.5 (*d*, C-8′) and 122.0 (*d*, C-9′), respectively. In addition, the spectra also showed two methylene carbons at δ_C 68.5 (*t*, C-1′) and δ_C 46.3 (*t*, C-3′), an acyl group at δ_C 168.1 (*s*, C-1) and one keto carbon at δ_C 204.5 (*s*, C-2′). On the basis of these data, **1** was concluded to be a caffeic acid derivative.

In the HMBC spectrum, the methoxyl signal (δ_H 3.88) showed a cross-peak with a quaternary carbon at δ_C 151.7 (C-7). This quaternary carbon showed correlation with two proton signals at δ_H 7.09 and 7.06 (H-5 and H-9, respectively). The HMBC spectrum also showed correlations between H-1′ (δ_H 4.86) with the acyl signal at δ_C 168.1 (C-1), and with the keto signal at δ_C 204.5 (C-2′). The signal at δ_H 3.63, which showed correlations with two quaternary carbons at δ_C 204.5 (C-2′) and 126.0 (C-4′) was assigned to H-3′. Since all proton and carbon signals have now been assigned, the structure of compound **1** must be 2′-oxo-3′-(3,4-dihydroxyphenyl)-propoxyl-3-(3-hydroxy-4-methoxyphenyl)-2*E*-propenoate.

Cimiracemate B (**2**) was obtained as a light brown powder. As for **1**, the molecular formula was determined to be $C_{19}H_{18}O_7$ based on a negative HR-ESIMS *m/z* 357.0974 (calc 357.0974 for $C_{19}H_{17}O_7$). Comparative analysis of the ^{1}H and ^{13}C NMR spectra of **2** and those of **1** showed them to be identical except for the signals at H-5 and H-8; and C-6 and C-7. The ^{1}H NMR signal at H-5 in **1** shifted downfield from δ_H 7.09 to δ_H 7.21 in **2**, while the H-8 signal in **1** shifted upfield from δ_H 6.94 to δ_H 6.83 in **2**. Moreover, the ^{13}C NMR signal at C-6 [δ_C 148.0 (*s*)] in **1** was shifted downfield to δ_C 150.9 (*s*) in **2**. Meanwhile, the C-7 in **1** shifted upfield from δ_C 151.7 (*s*) to δ_C 149.4 (*s*) in **2**. These chemical shift changes can be explained as being due to the exchange of two electronegative groups at C-6 and C-7, that is, the hydroxyl group at C-6 in **1** became a methoxyl group in **2**, and the methoxyl group in **1** was changed to a hydroxyl group in **2**. These assignments were confirmed by an HMBC experiment of **2**.

In the HMBC spectrum of **2**, the methoxyl signal (δ_H 3.89) showed a cross-peak with a quaternary carbon at δ_C 150.9 (C-6), which in turn showed correlation with the H-5 and H-8 signals at δ_H 7.21 (1H, *d*, $J = 1.9$ Hz) and 6.83 (1H, *d*, $J = 8.2$ Hz), respectively. H-8 also showed correlation with the C-4 quaternary carbon at δ_C 127.5. The HMBC spectrum also showed correlations between H-1′ (δ_H 4.86) and the acyl signal at δ_C 168.3 (C-1) and the keto signal at δ_C 204.6 (C-2′). The signal at δ_H 3.62, which showed correlations with the quaternary carbons at δ_C 204.6 (C-2′) and 126.0 (C-4′), was assigned to H-3′. On the basis of these observations, the structure of compound **2** was elucidated as 2′-oxo-3′-(3,4-dihydroxyphenyl)-propoxyl-3-(4-hydroxy-3-methoxyphenyl)-2*E*-propenoate.

Cimiracemate C (**3**), obtained as a light brown powder, showed a molecular formula of $C_{20}H_{20}O_8$ (negative HR-ESIMS *m/z* 387.1073 [calc. 387.1080 for $C_{20}H_{19}O_8$]). Since the molecular ion peak of compound **3** was 30 Da more than that of **1**, it likely contained an extra methoxyl group. UV absorptions were almost the same as compound **1**. Comparative analysis of the ^{1}H and ^{13}C NMR spectral data of **3** with those of **1** showed them to be very similar except for an additional methoxyl signal at δ_C 57.1 (*q*) and δ_H 3.33 (3H, *s*) in **3**, and the absence of a methylene signal at δ_C 46.4 (*t*) and δ_H 3.63 (2H, *s*) found in **1**. Instead, an oxygenated methine signal at δ_C 88.2 (*d*) and δ_H 4.79 (1H, *s*) was present in **3**. Moreover, with a methoxyl group at C-3′ in **3**, the ^{1}H chemical shift of another set of methylene protons (H-1′) in **1** shifted downfield from a singlet at δ_H 4.86 to two doublets at δ_H 4.94 (1H, *d*, $J = 17.5$) and 5.00 (1H, *d*, $J = 17.5$) in **3**. In the ^{13}C NMR, the chemical shift of the corresponding methylene carbon (C-1′) in **1** was shifted upfield by 1.6 ppm in **3**.

Besides the HMBC correlation of proton and carbon signals in the aromatic rings as shown in **1**, the proton signal of the methine at δ_H 4.79 (H-1′) showed correlation with a methyl carbon signal at δ_C 57.1 (*q*, OCH_3), with two methine signals at δ_C 115.5 (*d*, C-5′) and 120.7 (*d*, C-9′), with a quaternary carbon signal at δ_C 127.9 (*s*, C-4′), and with a ketone signal at δ_C 203.6 (C-2′). The ketone carbon also showed two cross-peaks with protons at δ_H 4.94 and 5.00. Therefore, the structure of compound **3** was determined as 2′-oxo-3′-methoxyl-3′-

(3,4-dihydroxyphenyl)-propoxyl-3-(3-hydroxy-4-methoxyphenyl)-2*E*-propenoate.

Cimiracemate D (**4**) was obtained as a light brown powder. The molecular formula was determined to be $C_{20}H_{20}O_7$ based on its negative HR-ESIMS *m*/*z* 387.1084 (calc. 387.1080 for C_{20} $H_{19}O_8$), which is the same as that of **3**. Comparative analysis of ^1H and ^{13}C NMR spectral data of **4** with those of **3** indicated they were identical except for ^1H NMR signals at H-5 and H-8 and ^{13}C NMR signals at C-6 and C-7. These differences were similar to the differences found between compounds **1** and **2**. The ^1H NMR signal at H-5 in **3** shifted downfield from δ_H 7.07 to δ_H 7.19 in **4** while the H-8 signal in **3** shifted upfield from δ_H 6.94 to δ_H 6.81 in **4**. Moreover, the ^{13}C NMR signal at C-6 [δ_C 148.1 (*s*)] in **3** shifted downfield to δ_C 150.8 (*s*) in **4**. Meanwhile, the C-7 in **3** shifted upfield from δ_C 151.7 (*s*) to δ_C 149.4 (*s*) in **4**. Therefore, compound **4** is a derivative of ferulic acid and was elucidated as 2′-oxo-3′-methoxyl-3′-(3,4-dihydroxyphenyl)-propoxyl-3-(3-hydroxy-4-methoxyphenyl)-2*E*-propenoate.

Cimiracemates A–D are phenylpropanoid ester dimers being reported for the first time from a member of the evolutionary primitive dicot family Ranunculaceae. A structurally related compound, coniferyl ferulate, was previously documented to be present in *Coreopsis parvifolia*, a member of the evolutionary advanced Asteraceae (Bohlmann and Zdero, 1977); as well as in *Angelica sinensis* (Apiaceae), a member of another evolutionary advanced taxon (Lin et al., 1998). The occurrence of these class of compounds in such divergent taxa suggest that they may be derived by analogous formation and are not suitable candidates as chemotaxonomic markers.

Although these compounds must be derived from two phenylpropanoid units, they appear to be formed via esterification rather than through phenol oxidative coupling as in the case of lignans. Therefore, cimiracemates **A**–**D** should be classified as phenylpropanoid ester dimers rather than as lignans.

3. Experimental

3.1. General

Mps uncorr. TLC precoated Kieselgel 60 F_{254} Si and RP-18 (0.25 mm, Merck). CC silica gel (mesh 230–400) eluted with $CHCl_3$–MeOH (gradient) or $CHCl_3$–acetone–H_2O (17:1:0.1), and CC RP-18 (Lobar Lichroprep, 40–63 μm, 25×310 mm, Merck) eluted with MeOH–H_2O (55:45) at the rate of 4 ml/min, 5% H_2SO_4 in *n*-BuOH and UV were used for detection of TLC. Semipreparative HPLC was carried out on a Waters 996 system equipped with a photodiode array detector on a Watrex GROM-Sil 120 ODS-4 HE semipreparative column (5 μm, 20×300 mm) with a flow rate of 6 ml/min. $[\alpha]_D$ in MeOH (Perkin-Elmer 241 polarimeter), UV in MeOH (DU-7 Spectrophotometer, Beckman), and IR on NaCl (FTIR, ATI Mattson Instruments Inc.) were obtained using the instruments indicated. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz, Bruker Avance 500) were recorded in CD_3OD using TMS as int. standard. Chemical shifts (δ) were expressed in ppm with reference to TMS. HR-ESIMS data were recorded on a QTOF system (Micromass, Manchester, UK).

3.2. Plant material

Cimicifuga racemosa (L.) Nutt. roots and rhizomes were collected in Rockbridge County, Virginia (June 1999), GPS coordinates 37 48.27 N×79 18.67 W, identified by Dr. G. Ramsey, Department of Biology, Lynchburg College, Lynchburg, Virginia, USA. Voucher specimens have been deposited at the Ramsey-Freer Herbarium at Lynchburg College, Lynchburg, Virginia, USA, at the Field Museum of Natural History Herbarium, Chicago, Illinois, USA. Voucher specimens (BC009) have also been deposited at the University of Illinois at Chicago Pharmacognosy Field Station, Downers Grove, Illinois, USA

3.3. Extraction and isolation

The air-dried, milled, rhizomes of *C. racemosa* (8 kg) were exhaustively extracted with MeOH, fractionated by successive partitions with EtOAc and 1-BuOH; the EtOAc fraction was applied to a silica gel column as previously described to afford eight fractions (I–VIII) (Chen et al., 2002a,b). Work-up of the green colored Fraction IV (2.3 g) by normal-phase Si gel CC, and gradient elution with increasing polarity of $CHCl_3$–MeOH afforded five sub-fractions (CR-4-SF-I to CR-4-SF-V). Due to their similar TLC profiles, subfractions CR-4-SF-II to CR-4-SF-IV were combined, and subjected to RP-18 low pressure CC and silica gel CC to yield isoferulic acid (230 mg), ferulic acid (40 mg), methyl caffeate (12 mg) and a mixture (CR-4-SF-II-A, 70 mg), which was subjected to semipreparative HPLC separation (C-18 column, isocratic: 37% acetonitrile in H_2O, 6ml/min) to yield other four fractions CR-4-SF-II-A-1 to CR-4-SF-II-A-4. Purification of CR-4-SF-II-A-3 on HPLC with 50% MeOH (6 ml/min) yielded compounds **1** (8 mg) and **2** (5 mg). Purification of the fraction CR-4-SF-II-A-4 on HPLC with a linear gradient solvent of 50–70% MeOH (6 ml/min, 40 min) gave compounds **3** (2.1 mg) and **4** (1.8 mg).

3.4. Cimiracemate A (*1*)

Light brown powder, mp 94–96 °C. UV λ_{max}^{MeOH} nm (log ϵ): 210.5 (4.26), 291.0 (3.77), 325.0 (3.96). IR ν_{max}^{NaCl}

cm^{-1}: 3403, 2940, 1705, 1608, 1512, 1442, 1264, 1162, 1131, 1023. ^1H NMR spectral data (500 MHz, CD_3OD): δ 6.36 (1H, *d*, $J=15.9$ Hz, H-2), 7.61 (1H, *d*, $J=15.9$ Hz, H-3), 7.09 (1H, *d*, $J=2.1$ Hz, H-5), 6.94 (1H, *d*, $J=8.3$ Hz, H-8), 7.06 (1H, *dd*, $J_{5,9}=2.1$ Hz, $J_{8,9}=8.3$ Hz, H-9), 4.86 (2H, *s*, H-1′), 3.63 (2H, *s*, H-3′), 6.68 (1H, *d*, $J=2.0$ Hz, H-5′), 6.73 (1H, *d*, $J=8.0$ Hz, H-8), 6.57 (1H, *dd*, $J_{5,9}=2.0$ Hz, $J_{8,9}=8.0$ Hz, H-9), 3.88 (3H, *s*, MeO-7); ^{13}C NMR spectra data (125 MHz, CD_3OD): δ 168.1 (*s*, C-1), 115.2 (*d*, C-2), 147.4 (*d,* C-3), 128.8 (*s*, C-4), 114.8 (*d*, C-5) 148.0 (*s*, C-6), 151.7 (*s*, C-7), 112.5 (*d*, C-8), 123.0 (*d*, C-9), 68.5 (*t*, C-1′), 204.5 (*s*, C-2′), 46.3 (*t*, C-3′), 126.0 (*s*, C-4′), 117.6 (*d*, C-5′), 146.6 (*s*, C-6′), 145.7 (*s*, C-7′), 116.5 (*d*, C-8′), 122.0 (*d*, C-9′), 56.4 (*q*, MeO-7). Negative ESI–MS *m*/*z* (relative intensity%): 357 (18)$[M]^-$, 193 (100), 178 (20), 163 (90), 149 (25), 134 (48); HR-ESIMS *m*/*z* 357.0974 (calc. 357.0974 for $C_{19}\ H_{17}O_7$).

3.5. Cimiracemate B (*2*)

Light brown powder, mp 86–88.5 °C. UV λ_{max}^{MeOH} nm (log ϵ): 208.5 (4.28), 327.5 (3.92). IR ν_{max}^{NaCl} cm^{-1}: 3396, 2930, 1708, 1600, 1519, 1448, 1217, 1172, 1125, 1030. ^1H NMR spectral data (500 MHz, CD_3OD): δ 6.42 (1H, *d*, $J=16.0$ Hz, H-2), 7.65 (1H, *d*, $J=16.0$ Hz, H-3), 7.21 (1H, *d*, $J=1.9$ Hz, H-5), 6.83 (1H, *d*, $J=8.3$ Hz, H-8), 7.09 (1H, *dd*, $J_{5,9}=1.9$ Hz, $J_{8,9}=8.2$ Hz, H-9), 4.86 (2H, *s*, H-1′), 3.62 (2H, *s*, H-3′), 6.68 (1H, *d*, $J=2.0$ Hz, H-5′), 6.73 (1H, *d*, $J=8.0$ Hz, H-8′), 6.57 (1H, *dd*, $J_{5,9}=2.0$ Hz, $J_{8,9}=8.0$ Hz, H-9′), 3.89 (3H, *s*, MeO-6); ^{13}C NMR spectra data (125 MHz, CD_3OD): δ 168.3 (*s*, C-1), 114.5 (*d*, C-2), 147.4 (*d,* C-3), 127.6 (*s*, C-4), 116.5 (*d*, C-5), 150.9 (*s*, C-6), 149.4 (*s*, C-7), 111.7 (*d*, C-8), 124.3 (*d*, C-9), 68.5 (*t*, C-1′), 204.6 (*s*, C-2′), 46.3 (*t*, C-3′), 126.0 (*s*, C-4′), 117.6 (*d*, C-5′), 146.6 (*s*, C-6′), 145.7 (*s*, C-7′), 116.5 (*d*, C-8′), 122.0 (*d*, C-9′), 56.4 (*q*, MeO-6). Negative ESI–MS *m*/*z* (relative intensity%): 357 (23)$[M]^-$, 313 (10%), 193 (100), 179 (45), 163 (70), 149 (70), 134 (68), HR–ESIMS *m*/*z* 357.0974 $[M]^-$ (calc. 357.0974 for $C_{19}\ H_{17}O_7$).

3.6. Cimiracemate C (*3*)

Light brown powder, mp 88–90 °C. $[\alpha]_D^{20}$ −6.82° (MeOH; *c* 0.147), UV λ_{max}^{MeOH} nm (log ϵ): 212.0 (4.35), 292.9 (3.87), 326.0 (4.09). IR ν_{max}^{NaCl} cm^{-1}: 3399, 2927, 1710, 1608, 1515, 1442, 1270, 1156. ^1H NMR spectral data (500 MHz, CD_3OD): δ 6.35 (1H, *d*, $J=15.9$ Hz, H-2), 7.59 (1H, *d*, $J=16.0$ Hz, H-3), 7.07 (1H, *d*, $J=2.0$ Hz, H-5), 6.94 (1H, *d*, $J=8.4$ Hz, H-8), 7.06 (1H, *dd*, $J_{5,9}=2.0$ Hz, $J_{8,9}=8.4$ Hz, H-9), 4.94 (1H, *d*, $J=17.5$ Hz, H-1′a), 5.00 (1H, *d*, $J=17.5$ Hz, H-1′b), 4.79 (H, *s*, H-3′), 6.78 (1H, *d*, $J=2.0$ Hz, H-5′), 6.79 (1H, *d*, $J=8.1$ Hz, H-8′), 6.72 (1H, *dd*, $J_{5,9}=2.0$ Hz, $J_{8,9}=8.1$ Hz, H-9′), 3.89 (3H, *s*, MeO-7), 3.33 (3H, *s*, MeO-3′). ^{13}C NMR spectra data (125 MHz, CD_3OD): δ 168.1 (*s*, C-1), 115.2 (*d*, C-2), 147.4 (*d,* C-3), 128.8 (*s*, C-4), 114.8 (*d*, C-5) 148.1 (*s*, C-6), 151.7 (*s*, C-7), 112.5 (*d*, C-8), 123.0 (*d*, C-9), 66.9 (*t*, C-1′), 203.6 (*s*, C-2′), 88.2 (*d*, C-3′), 127.9 (*s*, C-4′), 115.5 (*d*, C-5′), 147.4 (*s*, C-6′), 147.0 (*s*, C-7′), 116.5 (*d*, C-8′), 120.7 (*d*, C-9′), 56.4 (*q*, MeO-7), 57.1 (*q*, MeO-3′). Negative ESI–MS *m*/*z* (relative intensity%): 387 (8)$[M]^-$, 355 (33), 340 (10), 296 (30), 193 (100), 178 (45), 161 (38), 149 (27), 134 (37). HR–ESIMS *m*/*z* 387.1073 $[M]^-$ (calc. 387.1080 $C_{20}\ H_{19}O_8$).

3.7. Cimiracemate D (*4*)

Light brown powder, mp 100–102 °C. $[\alpha]_D^{20}$ −6.25° (MeOH; *c* 0.147), UV λ_{max}^{MeOH} nm (log ϵ): 212.0 (4.35), 326.0 (4.09). IR ν_{max}^{NaCl} cm^{-1}: 3387, 2979, 1710, 1601, 1520, 1481, 1271, 1156, 1029. ^1H NMR spectral data (500 MHz, CD_3OD): δ 6.40 (1H, *d*, $J=15.9$ Hz, H-2), 7.63 (1H, *d*, $J=16.0$ Hz, H-3), 7.19 (1H, *d*, $J=1.9$ Hz, H-5), 6.94 (1H, *d*, $J=8.1$ Hz, H-8), 7.06 (1H, *dd*, $J_{5,9}=1.9$ Hz, $J_{8,9}=8.1$ Hz, H-9), 4.94 (1H, *d*, $J=17.5$ Hz, H-1′a), 5.00 (1H, *d*, $J=17.5$ Hz, H-1′b), 4.79 (H, *s*, H-3′), 6.79 (1H, *d*, $J=1.9$ Hz, H-5′), 6.80 (1H, *d*, $J=7.9$ Hz, H-8′), 6.72 (1H, *dd*, $J_{5,9}=1.9$ Hz, $J_{8,9}=7.9$ Hz, H-9′), 3.88 (3H, *s*, MeO-6), 3.35 (3H, *s*, MeO-3′). ^{13}C NMR spectra data (125 MHz, CD_3OD): δ 168.5 (*s*, C-1), 114.5 (*d*, C-2), 147.8 (*d,* C-3), 127.6 (*s*, C-4), 116.5 (*d*, C-5), 150.8 (*s*, C-6), 149.4 (*s*, C-7), 111.8 (*d*, C-8), 124.4 (*d*, C-9), 66.9 (*t*, C-1′), 203.7 (*s*, C-2′), 88.2 (*d*, C-3′), 127.9 (*s*, C-4′), 115.5 (*d*, C-5′), 147.4 (*s*, C-6′), 145.0 (*s*, C-7′), 116.6 (*d*, C-8′), 120.0 (*d*, C-9′), 56.5 (*q*, MeO-6), 57.2 (*q*, MeO-3′). Negative ESI–MS *m*/*z* (relative intensity%): 387 (12)$[M]^-$, 355 (22), 337 (22), 296 (22), 193 (95), 178 (100), 175 (52), 161(40), 149 (20), 134 (40), HR–ESIMS *m*/*z* 387.1084 (calc. 387.1080 $C_{20}\ H_{19}O_8$).

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