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AMIDES FROM STEMS OF *ANNONA CHERIMOLA*

CHUNG-YI CHEN, FANG-RONG CHANG, HSIN-FU YEN† and YANG-CHANG WU*

Graduate Institute of Natural Products, Kaohsiung Medical College, Kaohsiung 807, Taiwan, R.O.C.
†National Museum of Natural Science, Taichung 404, Taiwan, R.O.C.

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Key Word Index— *Annona cherimola*; Annonaceae; stems; *N-cis*-caffeoyl-tyramine; dihydro-feruloyltyramine; *N-trans*-feruloylmethoxytyramine; *N-cis*-feruloylmethoxytyramine.

Abstract—Four new amides, *N-cis*-caffeoyltyramine, dihydro-feruloyltyramine, *N-trans*-feruloylmethoxytyramine and *N-cis*-feruloylmethoxytyramine, along with two known amides, *N-p*-coumaroyltyramine and *N-cis*-feruloyltyramine, were isolated from the fresh stem parts of *Annona cherimola*. Their structures were characterized and identified by spectral analysis. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Annona cherimola is a subtropical fruit tree cultivated in southern Taiwan, but which is indigenous to Ecuador and Peru. It has been used for the treatment of skin disease, especially for boils in folk medicine [1]. Previously, we have isolated two novel compounds, cherimoline [2] and cherinonaine [3] and 21 alkaloids, four kauranes, two amides (*N-trans*-feruloyltyramine and *N-trans*-caffeoyltyramine), one purine, one lactam amide and six steroids from this species [4]. As part of our continuing investigation of the phytochemical and bioactive compounds of Formosan Annonaceous plants, four new amides, *N-cis*-caffeoyltyramine (**1**), dihydro-feruloyltyramine (**2**), *N-trans*-feruloylmethoxytyramine (**3**) and *N-cis*-feruloylmethoxytyramine (**4**), together with two known amides, *N-p*-coumaroyltyramine (**5**) and *N-cis*-feruloyltyramine (**6**) were obtained by systematic extraction and isolation from the fresh stems of *A. cherimola*. In addition to the four new compounds **1**–**4**, compounds **5** and **6** were also isolated for the first time from this source.

RESULTS AND DISCUSSION

N-cis-caffeoyltyramine (**1**) was obtained as a yellow oil. Its molecular formula was established as $C_{17}H_{17}NO_4$ by HRFAB mass spectrometry *m/z* $[M+H]^+$ (found 300.1247, calcd 300.1236) and ^{13}C NMR. Two IR bands at 3500 and 1650 cm^{-1} and a signal appearing at δ 169.29 (*s*) in the ^{13}C NMR spectrum suggested that hydroxyl groups and an amide group might be present. Its UV spectrum exhibited several absorption maxima in the same regions as *N-trans*-caffeoyltyramine [5]; these underwent bathochromic shifts on adding base, suggesting that **1** should be a phenolic derivative of an amide. The ^1H NMR spectrum revealed an ABX pattern at δ 6.70 (1 H, *d*, $J=8.2$ Hz), δ 6.83 (1 H, *dd*, $J=8.2$, 2.0 Hz) and 7.04 (1 H, *d*, $J=2.0$ Hz) for H-8, H-9 and H-5, respectively, in the caffeic acid moiety. A downfield doublet at δ 6.56 ($J=12.6$ Hz) was assigned to the C-3 olefinic proton of the caffeic acid moiety showing *cis*-coupling with the C-2 olefinic protons, which appeared as a doublet at δ 5.77 ($J=12.6$ Hz). A typical AA′BB′ system was observed at δ 6.68 (2 H, *d*, $J=8.4$ Hz) and 6.99 (2 H, *d*, $J=8.4$ Hz) for H-5′, 7′ and H-4′, 8′, and two coupled triplets of methylene protons at δ 2.68 and δ 3.38 (each 2 H, *t*, $J=6.8$ Hz) for H-2′ and H-1′, for the tyramine moiety, respectively. ^{13}C NMR and DEPT experiments on **1** showed 17 resonance lines consisting of two methylenes, nine methines and six quaternary carbons (including a carbonyl signal at δ 169.29). The mass, UV, IR and ^1H NMR data suggested that the structure of this compound is a type of phenolic acid amide and that the hydroxyl groups should be located on the skeleton.

To confirm the structure, 2D NMR and NOESY spectra were run. Sequential correlations successfully established the existence of a pair of methylenes at δ 2.68 and 3.38, the δ of three aromatic protons of the ABX system, a pair of olefinic protons at δ 5.77 and 6.56 and the δ of four aromatic protons of an AA′BB′ system. NOESY confirmed the structure of *N-cis*-caffeoyltyramine, a new phenolic acid amide. The results are summarized in Fig. 1.

* Author to whom correspondence should be addressed.

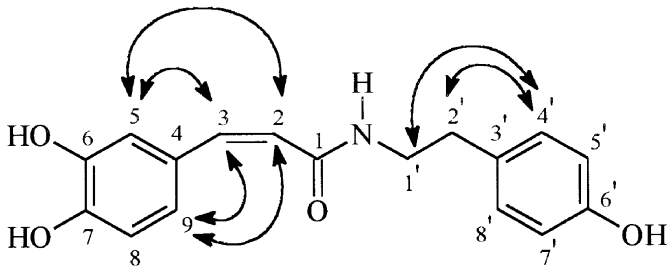


Fig. 1. NOESY experiments of *N-cis*-caffeoyltyramine (**1**).

Dihydro-feruloyltyramine (**2**) was obtained as a white powder. Its molecular formula was established as $C_{18}H_{21}NO_4$ by HREI mass spectrometry (found 315.1471, calcd 315.1470) and ^{13}C NMR. Two IR bands at 3300 and 1650 cm^{-1} and a signal appearing at δ 175.36 (s) in the ^{13}C NMR spectrum suggested that hydroxyl groups and an amide group might be present. The UV absorption maxima at 206, 255sh and 280 underwent bathochromic shifts on adding base, suggesting that **2** should be a phenolic derivative of an amide. The ^{1}H NMR spectrum revealed an ABX pattern at δ 6.79 (1 H, *d*, J=7.6 Hz), δ 6.62 (1 H, *dd*, J=8.0, 2.0 Hz) and 6.67 (1 H, *d*, J=1.6 Hz) for H-8, H-9 and H-5, two coupled triplets of methylene protons at δ 2.37 and δ 2.83 (each 2 H, *t*, J=7.6 Hz) for H-2 and H-3 in the dihydro-ferulic acid moiety, respectively. A typical AA′BB′ system was observed at δ 6.70 (2 H, *d*, J=8.4 Hz) and 6.87 (2 H, *d*, J=8.8 Hz) for H-5′,7′ and H-4′, 8′ and two coupled triplets of methylene protons at δ 2.62 and δ 3.39 (each 2 H, *t*, J=6.4 Hz) for H-2′ and H-1′, for the tyramine moiety, respectively. The ^{13}C NMR and DEPT experiments on **2** showed 18 resonance lines consisting of one methyl, four methylenes, seven methines and six quaternary carbons (including a carbonyl signal at δ 175.36). The mass, UV, IR and ^{1}H NMR data suggested that the structure was not a typical type of phenolic acid amide and that the *cis* double bond present in **1** was saturated on the phenolic acid moiety in **2**. Comparison of the spectral data with a known acid amide, *N-trans*-feruloyltyramine [4] revealed that both of the compounds were similar, except that the double bond of *N-trans*-feruloyltyramine was replaced by one pair of methylenes in **2**.

To confirm the structure, 2D NMR and NOESY spectra were run. Sequential correlations successfully established the existence of a pair of methylenes at δ 2.37 and 3.83, the δ of three aromatic protons of the ABX system, the methoxyl group at δ 3.83 correlating with δ 6.67 (1 H, *d*, J=1.6 Hz), a pair of methylenes at δ 2.62 and 3.39, and the δ of four aromatic protons of an AA′BB′ system. NOESY confirmed the structure of dihydro-feruloyltyramine, a new phenolic acid amide. The results are summarized in Fig. 2. This is the first example of a naturally occurring acid amide possessing a dihydro-ferulic acid moiety.

N-trans-feruloylmethoxytyramine (**3**) was obtained from MeOH as a white amorphous powder, mp 111–113°. Its molecular formula was established as $C_{19}H_{21}NO_5$ by HREI mass spectrometry (found 343.1411, calcd 343.1420) and ^{13}C NMR. Two IR bands at 3350 and 1650 cm^{-1} and a signal appearing at δ 169.19 (*s*) in the ^{13}C NMR spectrum suggested that hydroxy-groups and an amide group might be present. It showed a UV spectrum with strong absorption maxima at 319, 290 and 220 nm, indicating a highly conjugated system [6–8]; these underwent bathochromic shifts on adding base, suggesting that **3** should be a phenolic derivative of an amide. The ^{1}H NMR spectrum of **3** revealed an ABX pattern at δ 6.80 (1 H, *d*, J=8.4 Hz), δ 7.03 (1 H, *dd*, J=8.4, 2.0 Hz) and 7.21 (1 H, *d*, J=2.0 Hz) for H-8, H-9 and H-5 in the ferulic acid moiety, respectively. A downfield doublet at δ 7.44 (J=15.6 Hz) was assigned to the C-3 olefinic proton, on the ferulic acid moiety showing *trans*-coupling with the C-2 olefinic proton, which appeared as a doublet at δ 6.41 (J=15.6 Hz). Another ABX pattern was observed at δ 6.67 (1 H,

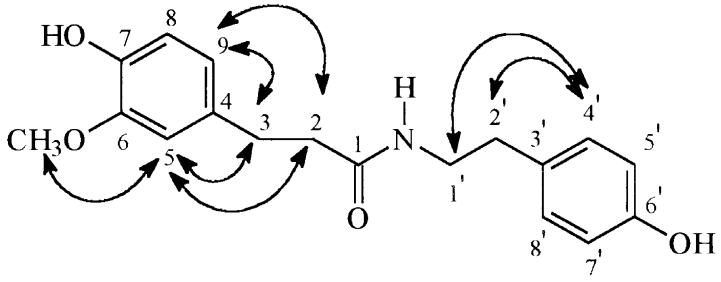


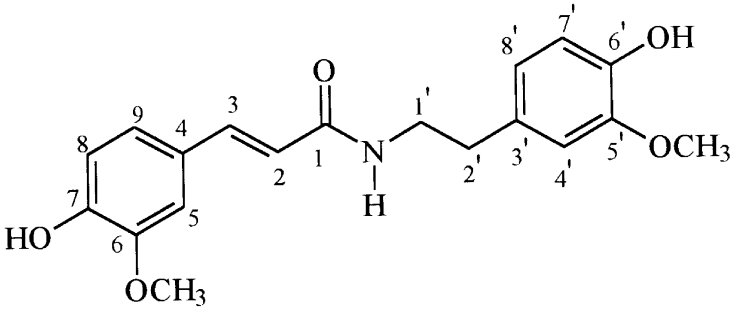
Fig. 2. NOESY experiments of dihydro-feruloyltyramine (**2**).

dd, $J=8.0$, 2.0 Hz), δ 6.73 (1 H, *d*, $J=8.0$ Hz) and 6.82 (1 H, *d*, $J=2.0$ Hz) for H-8′, H-7′ and H-4′ in the methoxytyramine moiety, respectively. Two coupled triplets of methylene protons at δ 2.77 and δ 3.49 (each 2 H, *t*, $J=7.2$ Hz) were ascribed to H-2′ and H-1′, in the methoxytyramine moiety, respectively. ^{13}C NMR and DEPT experiments on **3** showed 19 resonance lines consisting of two methyls, two methylenes, eight methines and seven quaternary carbons (including a carbonyl signal at δ 169.19). The mass, UV, IR and ^{1}H NMR data suggested that **3** is a type of phenolic acid amide and that the position of methoxyl and hydroxyl groups should be located on the skeleton.

In order to elucidate the position of aromatic substitution, a NOESY experiment was performed on **3**. This revealed that the methoxyl protons were at δ 3.88 on the ferulic acid moiety, with a significant degree of NOE enhancement being observed for H-5 (at δ 7.21) with a negligible degree of NOE enhancement being observed for H-9 (at δ 7.03). The other methoxyl protons at δ 3.82 on the methoxytyramine moiety revealed a significant degree of NOE enhancement for H-4′ (at δ 6.82) with a negligible degree of NOE enhancement being observed for H-8′ (at δ 6.67). These observations confirmed the structure of **3** as the new phenolic acid amide, *N-trans*-feruloylmethoxytyramine.

N-cis-feruloylmethoxytyramine (**4**) was obtained from MeOH as a white amorphous powder, mp 107–110°. Its molecular formula was established as $C_{19}H_{21}NO_5$ by HREI mass spectrometry (found 343.1416, calcd 343.1420) and ^{13}C NMR. Two IR bands at 3350 and 1650 cm^{-1} and a signal appearing at δ 169.23 (*s*) in the ^{13}C NMR spectrum suggested that hydroxyl groups and an amide group might be present. It showed a UV spectrum with strong absorption maxima at 319, 290 and 220 nm, indicating a highly conjugated system [6–8]; these underwent bathochromic shifts on adding base, suggesting that **4** should be a phenolic derivative of an amide. The ^{1}H NMR spectrum revealed an ABX pattern at δ 6.73 (1 H, *d*, $J=8.4$ Hz), δ 6.93 (1 H, *dd*, $J=8.4$, 2.0 Hz) and 7.36 (1 H, *d*, $J=2.0$ Hz) for H-8, H-9 and H-5 in the ferulic acid moiety, respectively. A downfield doublet at δ 6.61 ($J=12.8$ Hz) was assigned to the C-3 olefinic proton of the ferulic acid moiety showing *cis*-coupling with the C-2 olefinic proton, which appeared as a doublet at δ 5.82 ($J=12.8$ Hz). Another ABX pattern was at δ 6.61 (1 H, *dd*, $J=8.0$, 2.0 Hz), 6.70 (1 H, *d*, $J=8.0$ Hz) and 6.77 (1 H, *d*, $J=2.0$ Hz) for H-8′, H-7′ and H-4′ in the methoxytyramine moiety, respectively. Two coupled triplets of methylene protons were at δ 2.71 and δ 3.42 (each 2 H, *t*, $J=7.2$ Hz) for H-2′ and H-1′, in the methoxytyramine moiety, respectively. ^{13}C NMR and DEPT experiments on **4** showed 19 resonance lines consisting of two methyls, two methylenes, eight methines and seven quaternary carbons (including a carbonyl signal at δ 169.23). The mass, UV, IR and ^{1}H NMR data again suggested that **4** was a type of phenolic acid amide, with the methoxyl and hydroxyl groups located on the skeleton (Fig. 3).

In order to elucidate the position of the aromatic substitution, a NOESY experiment was performed on **4**. This revealed that the methoxyl protons were at δ



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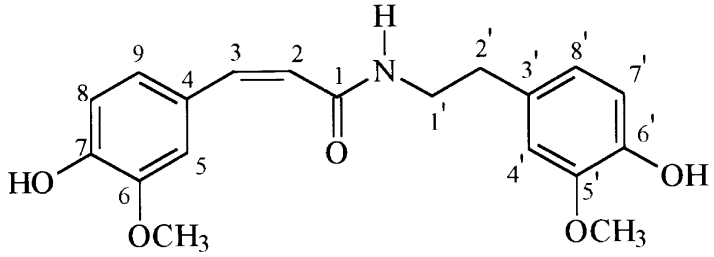

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Fig. 3. The structures of *N-trans*-feruloylmethoxytyramine (**3**) and *N-cis*-feruloylmethoxytyramine (**4**).

3.83 on the ferulic acid moiety, with a significant degree of NOE enhancement being observed for H-5 (at δ 7.36), with a negligible degree of NOE enhancement being observed for H-9 (at δ 6.93). The other methoxyl protons at δ 3.79 on the methoxytyramine moiety showed a significant degree of NOE enhancement for H-4′ (at δ 6.77), with a negligible degree of NOE enhancement being observed for H-8′ (at δ 6.61). The ^{1}H and ^{13}C NMR data were comparable to those of *N-trans*-feruloylmethoxytyramine (**3**), except for the existence of a *cis*-double bond. These observations established the structure of **4** as the new phenolic acid amide, *N-cis*-feruloylmethoxytyramine.

N-p-coumaroyltyramine (**5**) and *N-cis*-feruloyltyramine (**6**), were also isolated and their identities established by IR, mass spectrometric, ^{1}H and ^{13}C NMR studies [7, 9] and, finally, by TLC comparison with authentic samples. As shown in the previous paper [10], *N-trans*-feruloyltyramine, *N-p*-coumaroyltyramine (**5**) and *N-trans*-caffeoyltyramine showed significant inhibitory effects on the aggregation of rabbit platelets induced by thrombin, arachidonic acid, collagen and PAF. In particular, complete inhibition was observed in arachidonic acid-induced platelet aggregation by these compounds.

EXPERIMENT

General

Mps are uncorr. ^{1}H NMR were recorded 400 and 200 MHz, and ^{13}C NMR at 400 MHz and 100 MHz, in $CDCl_3$ using TMS as int. standard. EIMS were at 70 eV. Silica gel 60 (Macherey-Nagel and Merck), active charcoal (Wako) and Sephadex LH-20 (Pharmacia) were used for CC. Precoated silica gel (Macherey-Nagel, SIL G-25 UV254, 0.25 mm) was used for analytical TLC and precoated silica gel (Macherey-Nagel, SIL G/UV254, 0.25 mm) were used for prep. TLC.

Plant material

Annona cherimola Mill. was collected from Chia-Yi, Taiwan, in September 1995. A voucher specimen is deposited in the Graduate Institute of Natural Products, Kaohsiung Medical College, Kaohsiung, Taiwan, Republic of China.

Extraction and isolation

Fresh stems (4 kg) were extracted repeatedly with MeOH at room temp. The combined MeOH extracts were evap. under red. pres. and partitioned to yield $CHCl_3$ and aq. extracts. The bases in the $CHCl_3$ soln were extracted with 3% HCl. The remaining $CHCl_3$ soln was evapd to give a greenish viscous residue. The aq. extracts were partitioned with *n*-BuOH and gave *n*-BuOH and aq. extracts. The concd $CHCl_3$ extract was chromatographed over silica gel using hexane-Me_2CO as eluent to produce 24 fractions. Fr. 15 (1.03 g) eluted with hexane-Me_2CO (10:1) was further separated using silica gel CC and prep. TLC (hexane-Me_2CO (10:1)) and gave dihydro-feruloyltyramine (**2**) (4 mg). Fr. 16 (2.51 g) eluted with hexane-Me_2CO (5:1) was further separated using silica gel CC and prep. TLC (EtOAc-hexane (3:1)) and gave *N-trans*-feruloylmethoxytyramine (**3**) (12 mg) and *N-cis*-feruloylmethoxytyramine (**4**) (5 mg), respectively. Fr. 18 (1.54 g) eluted with hexane-EtOAc-Me_2CO (5:1:1) was further separated using silica gel CC and prep. TLC (hexane-EtOAc-Me_2CO (5:1:1)) and gave *N-cis*-caffeoyltyramine (**1**) (5 mg). The n-BuOH layer was concd and chromatographed over an active carbon column (30 × 5 cm) using MeOH-$CHCl_3$ as eluent to produce 10 frs. Fr. 2 (2.47 g) eluted with $CHCl_3$-MeOH (10:1) was further purified by silica gel CC using the same solvent system to obtain *N-p*-coumaroyltyramine (**5**) (11 mg). Fr. 9 (1.57 g) eluted with hexane-EtOAc (1:1) was further purified by silica gel CC using the same solvent system to obtain *N-cis*-feruloyltyramine (**6**) (6 mg).

N-cis-caffeoyltyramine (***1***)

Yellow oil, silica gel TLC (hexane-EtOAc-Me_2CO, 5:1:1), R_f 0.58. UV (EtOH) λ max(log ϵ) 203 (2.43), 220 (sh, 3.36), 280 (2.53), 310 (3.21) nm. IR (neat) ν max 3400 (OH), 1650 (C=O), 1590, 1515, 1440 cm^{-1}. ^{1}H NMR (MeOH, 400 MHz) *caffeoyl moiety*: δ 5.77 (1 H, *d*, J=12.6 Hz, H-2), 6.56 (1 H, *d*, J=12.6 Hz, H-3), 6.70 (1 H, *d*, J=8.2 Hz, H-8), 6.83 (1 H, *dd*, J=8.2, 2.0 Hz, H-9), 7.04 (1 H, *d*, J=2.0 Hz, H-5); *tyramine moiety*: δ 2.68 (2 H, *t*, J=6.8 Hz, H-2′), 3.38 (2 H, *t*, J=6.8 Hz, H-1′), 6.68 (2 H, *t*, J=8.4 Hz, H-5′ and H-7′), 6.99 (2 H, *d*, J=8.6 Hz, H-4′ and H-8′). ^{13}C NMR (MeOH, 100 MHz) *caffeoyl moiety*: δ 115.1 (C-5), 116.5 (C-8), 118.5 (C-2), 122.2 (C-9), 128.3 (C-4), 142.2 (C-3), 146.7 (C-6), 148.7 (C-7), 169.3 (C-1); *tyramine moiety*: 35.8 (C-2′), 42.6 (C-1′), 116.3 (C-5′ and C-7′), 130.8 (C-4′ and C-8′), 131.4 (C-3′), 157.0 (C-6′). FABMS m/z (rel. int.): $[M+H]^+$ 300 (4), 207 (9), 163 (6), 147 (1), 133 (22), 115 (100), 105 (8), 93 (2). HRFABMS m/z $[M+H]^+$ 300.1247 (300.1236 calcd for $C_{17}H_{18}NO_4$).

Dihydro-feruloyltyramine (***2***)

White amorphous powder, mp >300°. Silica gel TLC (hexane-Me_2CO, 10:1) R_f 0.63. UV (EtOH) λ max(log ϵ) 206 (2.73), 255 (sh, 3.65), 280 (2.34) nm. IR (neat) ν max 3300 (OH), 1650 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) *dihydro-feruloyl moiety*: δ 2.37 (2 H, *t*, J=7.2 Hz, H-2), 2.83 (2 H, *t*, J=7.6 Hz, H-3), 3.83 (3 H, *s*, MeO-6), 6.62 (1 H, *dd*, J=8.0, 2.0 Hz, H-9), 6.67 (1 H, *d*, J=1.6 Hz, H-5), 6.79 (1 H, *d*, J=7.6 Hz, H-8); *tyramine moiety*: δ 2.62 (2 H, *t*, J=6.4 Hz, H-2′), 3.39 (2 H, *t*, J=6.4 Hz, H-1′), 6.70 (2H, *t*, J=8.4 Hz, H-5′ and H-7′), 6.87 (2 H, *d*, J=8.8 Hz, H-4′ and H-8′). ^{13}C NMR ($CDCl_3$,

100 MHz) *dihydro-feruloyl moiety*: δ 32.6 (C-3), 39.4 (C-2), 56.4 (6-OCH_3), 175.4 (C-1), 113.2 (C-5), 116.3 (C-8), 121.9 (C-9), 133.8 (C-4), 148.5 (C-6), 148.9 (C-7); *tyramine moiety*: δ 35.7 (C-2′), 42.3 (C-1′), 116.2 (C-5′ and C-7′), 130.7 (C-4′ and C-8′), 131.3 (C-3′), 156.8 (C-6′); EIMS *m/z* (rel. int.): $[M]^+$ 315 (7), 195 (69), 177 (21), 150 (36), 137 (100), 120 (67), 107 (60). HREIMS *m/z* $[M]^+$ 315.1471 (315.1470 calcd for $C_{18}H_{21}NO_4$).

N-trans-feruloylmethoxytyramine (***3***)

White needles, mp 111–113°. Silica gel TLC (EtOAc-hexane, 3:1) R_f 0.55. UV (EtOH) λ max(log ϵ) 220 (3.42), 290 (2.67), 319 (3.15) nm. IR (KBr) ν max: 3350 (OH), 1650 (C═O) cm^{-1}. ^1H NMR: (MeOH, 400 MHz) *feruloyl moiety*: δ 6.41 (1 H, *d*, *J* = 15.6 Hz, H-2), 7.44 (1 H, *d*, *J* = 15.6 Hz, H-3), 6.80 (1 H, *d*, *J* = 8.4 Hz, H-8), 7.03 (1 H, *dd*, *J* = 8.4, 2.0 Hz, H-9), 7.21 (1 H, *d*, *J* = 2.0 Hz, H-5); *methoxytyramine moiety*: δ 2.77 (2 H, *t*, *J* = 7.2 Hz, H-2′), 3.49 (2 H, t, *J* = 7.2 Hz, H-1′), 3.82 (3 H, *s*, MeO-5′), 6.67 (1 H, *dd*, *J* = 8.0, 2.0 Hz, H-8′), 6.73 (1 H, *d*, *J* = 8.0 Hz, H-7′), 6.82 (1 H, *d*, *J* = 2.0 Hz, H-4′). ^{13}C NMR: (MeOH, 100 MHz) *feruloyl moiety*: δ 56.4 (6-OCH_3), 111.6 (C-5), 116.5 (C-8), 118.8 (C-2), 123.2 (C-9), 132.1 (C-4), 142.0 (C-3), 149.0 (C-7), 149.9 (C-6), 169.2 (C-1); *methoxytyramine moiety*: 36.2 (C-2′), 42.5 (C-1′), 56.4 (5′-OCH_3), 113.5 (C-4′), 116.2 (C-7′), 122.3 (C-8′), 128.3 (C-3′), 146.1 (C-6′), 149.3 (C-5′). EIMS *m/z* (rel. int.): $[M]^+$ 343 (4), 193 (12), 177 (41), 151 (14), 150 (100), 145 (20), 137 (14). HREIMS *m/z* $[M]^+$ 343.1411 (343.1420 calcd for $C_{19}H_{21}NO_5$).

N-cis-feruloylmethoxytyramine (***4***)

White needles, mp 107–110°. Silica gel TLC (EtOAc-hexane, 3:1), R_f 0.54. UV (EtOH) λ max(log ϵ) 222 (3.47), 290 (2.64), 319 (3.20) nm. IR (KBr) ν max: 3350 (OH), 1650 (C═O) cm^{-1}. ^1H NMR: (MeOH, 400 MHz) *feruloyl moiety*: δ 5.82 (1 H, *d*, *J* = 12.8 Hz, H-2), 6.61 (1 H, *d*, *J* = 12.8 Hz, H-3), 6.73 (1 H, *d*, *J* = 8.4 Hz, H-8), 6.93 (1 H, *dd*, *J* = 8.4, 2.0 Hz, H-9), 7.36 (1 H, *d*, *J* = 2.0 Hz, H-5); *methoxytyramine moiety*: δ 2.71 (2 H, *t*, *J* = 7.2 Hz, H-2′), 3.42 (2 H, *t*, *J* = 7.2 Hz, H-1′), 3.79 (3 H, *s*, MeO-5′), 6.61 (1 H, *dd*, *J* = 8.0, 2.0 Hz, H-8′), 6.70 (1 H, *d*, *J* = 8.0 Hz, H-7′), 6.77 (1 H, *d*, *J* = 2.0 Hz, H-4′). ^{13}C NMR: (MeOH, 100 MHz) *feruloyl moiety*: δ 56.4 (6-OCH_3), 111.6 (C-5), 116.5 (C-8), 118.7 (C-2), 123.2 (C-9), 132.1 (C-4), 142.1 (C-3), 149.0 (C-7), 149.9 (C-6), 169.2 (C-1); *methoxytyramine moiety*: 36.2 (C-2′), 42.5 (C-1′), 56.4 (5′-OCH_3), 113.5 (C-4′), 116.2 (C-7′), 122.3 (C-8′), 128.2 (C-3′), 146.1 (C-6′), 149.4 (C-5′). EIMS *m/z* (rel. int.): $[M]^+$ 343 (6), 193 (15), 177 (30), 151 (18), 150 (100), 145 (23), 137 (10). HREIMS m/z $[M]^+$ 343.1416 (343.1420 calcd for $C_{19}H_{21}NO_5$).

N-p-coumaroyltyramine (***5***)

White powder, mp 235–238°. Silica gel TLC ($CHCl_3$-MeOH, 10:1), R_f 0.55). Characterized by spectral (UV, IR, ^1H NMR MS) analysis and comparison with lit. data [7].

N-cis-feruloyltyramine (***6***)

Pale yellow oil. Silica gel TLC (EtOAc-hexane, 1:1) R_f 0.45). Characterized by spectral (UV, IR, ^1H NMR, MS) analysis and comparison with lit. data [9].

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