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Characterization of cross-linked hydroxycinnamic acid amides isolated from potato common scab lesions

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Abstract

Four feruloyl amides, *N-trans*-feruloyloctopamine (**1**), *N-cis*-feruloyloctopamine (**2**), *N-trans*-feruloyltyramine (**3**), *N-cis*-feruloyltyramine (**4**), a cross-linked *N-trans*-feruloyltyramine dimer (**5**), and a cross-linked *N-cis*-feruloyltyramine dimer (**6**) were isolated from potato common scab lesions. The compounds were purified by TLC and characterized by a combination of ^{1}H and ^{13}C NMR spectroscopic techniques. The presence of an accompanying minor complex of cross-linked dimers containing both feruloyltyramines and feruloyloctopamines was also demonstrated. This is the first characterization of cross-linked hydroxycinnamic acid amides associated with wound healing in potato (*Solanum tuberosum*) tubers.

Keywords: Hydroxycinnamic acid amides; *Solanum tuberosum*; Common scab; *Streptomyces scabies*; Grossamide

1. Introduction

Common scab of potato (*Solanum tuberosum*) is predominantly attributed to infection by the soil bacterium *Streptomyces scabies* and represents a disease of major economic importance in many potato producing areas of the world (Loria et al., 1997; Hill and Lazarovits, 2005). Host-interaction studies have confirmed the involvement of a phytotoxin named thaxtomin A as an essential factor in the disease process (King et al., 1989, 1992; Loria et al., 1995; Kinkel et al., 1998; Healy et al., 2000). This significant discovery has provided a new means of selecting for scab resistance in potatoes (Lim and Khu, 1999; Luckman and Wilson, 2000) and precise methodologies for distinguishing between pathogenic and non-pathogenic isolates (King et al., 1991; Loria et al., 1997; Healy et al., 2000). Control measures however are still relatively inadequate and inconsistent (McKenna et al., 2001). As a consequence, the utilization of potato cultivars with resistance to infection by *Streptomyces scabies* inevitably offers one of the best strategies available for managing common scab.

Scab infection occurs mainly through the lenticels (breathing pores) of immature tubers and one aspect of cultivar resistance appears to be associated with the effectiveness of underlying wound periderm to wall off the infected portions (Darling, 1937; Spooner and Hammerschmidt, 1992). Development of this wound periderm results in the corky raised or pitted lesions characteristic of potato common scab. Suberization, the name given to this deposition of modified cell walls in the periderm is characterized by both poly-phenolic and poly-aliphatic domains (reviews by Bernards and Lewis, 1998; Bernards, 2002). With respect to the poly-phenolic domains, previous studies have demonstrated the synthesis and integration into cell walls of

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hydroxycinnamic acid amides as an early response of potato tubers to fungal attack (Clarke, 1982) or wounding (Negrel et al., 1993; Negrel et al., 1996). These compounds seemingly contribute to the formation of a poly-phenolic barrier which makes the cell walls more resistant to enzyme attack. We now report the isolation and characterization of several new cross-linked hydroxycinnamic acid amides which may function as intermediates in the barrier formation process. These compounds were first detected during isolations of the phytotoxin thaxtomin A from scab lesions of field infected potatoes.

2. Results and discussion

Fractionation by reversed-phase TLC of the acetone soluble extracts from potato common scab lesions (cv. Green Mountain) produced three major and one minor band which exhibited a blue fluorescence when exposed to UV light. Upon further fractionation by silica gel TLC each major band furnished two quite complementary products in an approximate 3–1 ratio. Table 1 summarizes chromatographic data for these products. The product pairs were designated compounds **1**–**6** based on their relative order of elution on reversed-phase TLC plates. Only compounds **1**–**4** were detectable in non-infected material. Utilizing two-dimensional correlated ^{1}H and ^{13}C NMR techniques, compounds **4** and **3** were unequivocally identified as the geometric isomers *cis* and *trans*-feruloyltyramine, respectively. The structures of these compounds are illustrated in Fig. 1 and their spectroscopic data was consistent with values reported in the literature (Munoz et al., 1996; Chang and Chen, 2001). Two-dimensional ^{1}H and ^{13}C NMR spectroscopic techniques were also utilized to characterize compounds **2** and **1** as the geometric isomers *cis* and *trans*-feruloyloctopamine, respectively. The structures of these compounds are likewise illustrated in Fig. 1. The NMR and MS properties of *trans*-feruloyloctopamine (**1**) were found consistent with those reported in the literature (Lee et al., 2004) but to our knowledge spectroscopic data for *cis*-feruloyloctopamine (**2**) has not been reported previously. We have therefore listed the contrasting ^{1}H and ^{13}C NMR spectroscopic data for both compounds in Table 2.

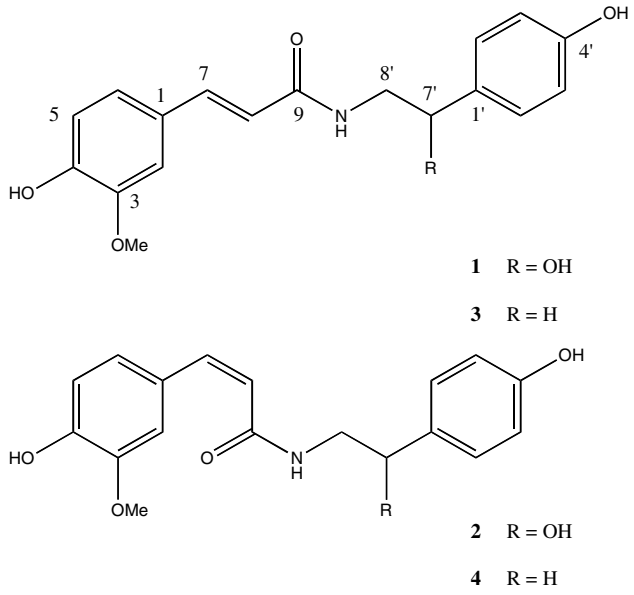

Fig. 1. Structural formulas of compounds **1**–**4**.

Classification of compounds **6** and **5** as another *cis*–*trans* pair of geometrical isomers containing conjugated carbonyl groups was inherent in their respective ^{1}H and ^{13}C NMR spectra with characteristic resonances easily correlated by HMBC at δ_C 167.44 ($\delta_H = 6.48$, 7.41)

Table 1
Summary of chromatographic data for compounds **1**–**6** and the mixed HCAA dimers

Compound	TLC R_f values		HPLC R_t (min)
	Silica gel	RP-C_{18}	
1	0.34	0.79	3.58
2	0.36	0.79	3.58
3	0.47	0.68	6.81
4	0.49	0.68	6.81
5	0.46	0.57	8.59
6	0.44	0.57	8.59
HCAA mixed dimers	0.17, 0.19	0.71	9.19–9.87

Table 2
^{13}C and ^{1}H NMR data for compounds **1** and **2**

Pos	**1**		**2**	
	δ_C mult[a]	δ_H mult (*J*, Hz)	δ_C mult[a]	δ_H mult (*J*, Hz)
1	128.10 *s*		128.30 *s*	
2	111.23 *d*	7.19 *d* (2.0)	114.51 *d*	7.90 *d* (2.0)
3	148.59 *s*		147.68 *s*	
4	149.21 *s*		148.31 *s*	
5	116.04 *d*	6.84 *d* (8.2)	115.21 *d*	6.78 *d* (8.2)
6	122.64 *d*	7.06 *ddd* (8.2, 2.0, 0.5)	125.51 *d*	7.12 *ddd* (8.2, 2.0, 0.5)
7	140.72 *d*	7.46 *d* (15.5)	138.40 *d*	6.58 *d* (12.9)
8	119.73 *d*	6.59 *d* (15.5)	121.73 *d*	5.88 *d* (12.9)
9	167.30 *s*		168.23 *s*	
1′	135.09 *s*		135.03 *s*	
2′	128.00 *d*	7.23 *d* (8.5)	127.99 *d*	7.21 *d* (8.6)
3′	115.70 *d*	6.79 *d* (8.5)	115.74 *d*	6.78 *d* (8.6)
4′	157.51 *s*		156.70 *s*	
5′	115.70 *d*	6.79 *d* (8.5)	115.74 *d*	6.78 *d* (8.6)
6′	128.00 *d*	7.23 *d* (8.5)	127.99 *d*	7.21 *d* (8.6)
7′	73.63 *d*	4.73 *dd* (8.0, 3.8)	73.44 *d*	4.72 *dd* (7.6, 3.8)
8′	48.72 t	3.35 *ddd* (13.8, 7.8, 5.3) 3.59 *ddd* (13.8, 3.8, 5.3)	48.58 *t*	3.36 *ddd* (13.4, 8.2, 5.3) 3.52 *ddd* (13.6, 6.6, 4.1)
OMe	56.10 *q*	3.88 *s*	56.20 *q*	3.84 *s*
NH		7.28 br s		7.28 br s

[a] Multiplicity derived from DEPT and HMQC spectra.

for compound **5** and δ_C 167.18 ($\delta_H = 5.87$, 6.57) for compound **6**. Further spectroscopic analysis using a combination of 2D NMR techniques (DEPT, HMQC and HMBC) indicated the presence of two tyramine moieties, one tri-substituted aromatic group and one tetra-substituted aromatic group per compound. Most evident also were correlated ^{1}H and ^{13}C NMR signals at δ_C 88.88 ($\delta_H = 6.03$) and 57.69 ($\delta_H = 4.18$) for compound **5** and δ_C 88.86 ($\delta_H = 5.99$) and 58.16 ($\delta_H = 4.20$) for compound **6**. Such resonances are comparable to those associated with the phenylcoumaran-type linkages displayed in suberin (Bernards et al., 1995), lignin (Ralph et al., 1992) and the hordatine phytoalexins (Stoessl, 1967). The nature of these proton signals, a pair of doublets ($J = 8.5$ Hz) for compound **5** and ($J = 7.8$ Hz) for compound **6** suggested a *cis* relationship for H-7′ and H-8′. These relative stereochemical assignments were subsequently confirmed (see Li et al., 1998) by 2 D NOESY which showed clear correlations between H-7′–H-8′, H-7′–H-2′, H-7′–H-6′, H-8′–H-2′ and H-8–H-6′ for both compounds. No attempt was made to assign the absolute stereochemistry.

Phenylcoumaran-type linkages are thought to occur via a peroxidase/H_2O_2 mediated free radical coupling of hydroxycinnamic acids and their derivatives (Bernards et al., 1995). Intermediate quinone methides produced from radical-coupling reactions involving the β-carbon typically undergo nucleophilic attack at the α-position (Ralph et al., 1992). The involvement of feruloyltyramine moieties in such a process could generate the homo-dimer structures assigned to compounds **5** and **6** (Fig. 2). Mass spectral data indicated molecular formulas of $C_{36}H_{36}N_2O_8$ in accord with these assignments. Subsequent literature searches revealed that a plant metabolite called Grossamide had previously been isolated from a number of other sources (Yoshihara et al., 1981; Sakakibara et al., 1991; Lajide et al., 1995; Santos et al., 1996; Li et al., 1998; Seca et al., 2001) and assigned a structure similar to that proposed for compound **5**. To our knowledge, *cis*-grossamide (**6**) has not been previously characterized and we have listed the contrasting ^{13}C NMR spectral data for both compounds in Table 3.

Further purification by normal-phase TLC of the minor band from the reversed-phase TLC fractions again yielded a major and a minor blue fluorescent band. ^{1}H NMR spectroscopic data of the major band confirmed the presence of compounds that contained conjugated double bonds with a *trans* configuration. The ^{1}H NMR spectroscopic also exhibited resonances comparable to those associated with phenylcoumaran type linkages and the presence of octopamine and tyramine groups. Mass spectral data and a further assessment of the ^{1}H NMR spectroscopic data confirmed a mix of two compounds that appeared to be the products of a cross-linking reaction between feruloyltyramine and feruloyloctapamine groups. A similar assessment of the minor blue fluorescent band from the normal-phase fractionation also indicated a mix of two compounds containing cross-linked feruloyltyramine and feruloyloctopamine groups and conjugated double bonds with a *cis* configuration. The presence of two dimeric products in each fluorescent band could arise from the two possible sequences for cross-linking i.e., feruloyltyramine to feruloyloctopamine and feruloyloctopamine to feruloyltyramine. Due to the paucity of this material, however, further structural elucidations were not pursued.

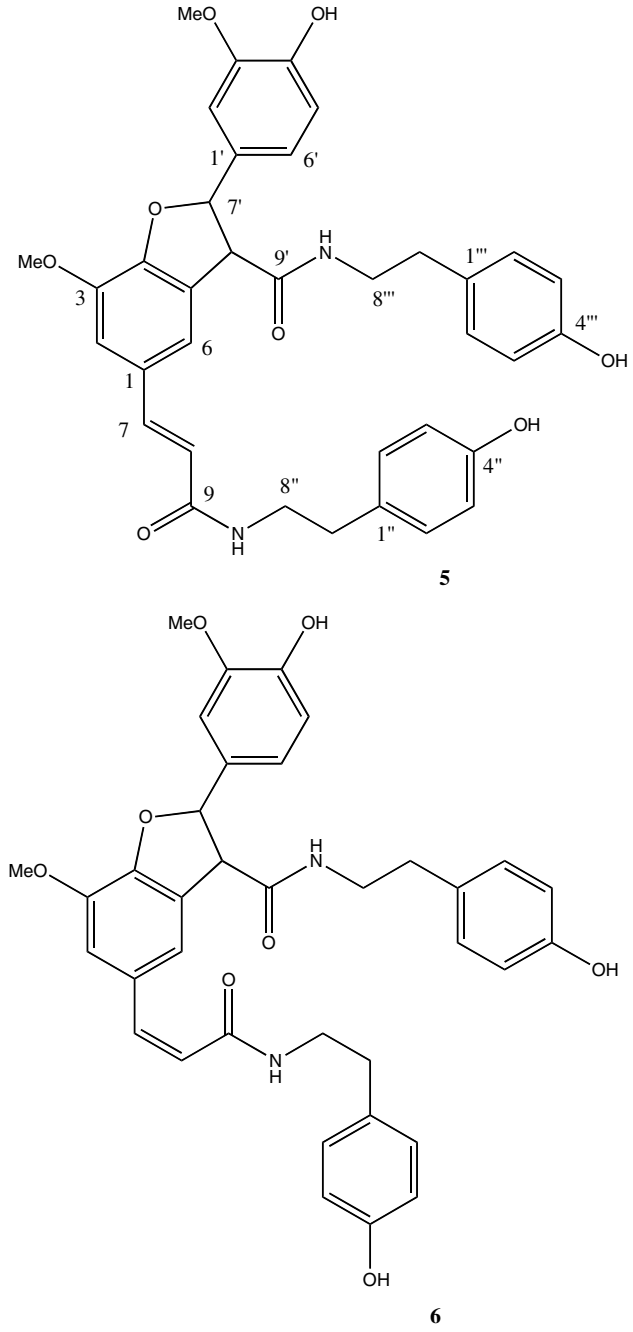

Fig. 2. Structural formulas of compounds **5** and **6**.

Table 3
^{13}C NMR data for compounds **5** and **6** (δ_C mult[a])

Carbon no.	5	6
Phenylpropyls		
1	129.57 *s*	130.14 *s*
2	111.16 *d*	115.88 *d*
3	145.59 *s*	144.67 *s*
4	150.58 *s*	149.61 *s*
5	129.31 *s*	128.25 *s*
6	119.02 *d*	120.08 *d*
7	141.30 *d*	137.71 *d*
8	119.23 *d*	122.91 *d*
9	167.44 *s*	167.18 *s*
1′	132.62 *s*	133.06 *s*
2′	110.65 *d*	110.47 *d*
3′	148.50 *s*	148.45 *s*
4′	147.75 *s*	147.60 *s*
5′	115.86 *d*	115.81 *d*
6′	119.93 *d*	119.71 *d*
7′	88.88 *d*	88.86 *d*
8′	57.69 *d*	58.16 *d*
9′	170.16 *s*	170.69 *s*
3-OMe	56.33 *q*	56.36 *q*
3′-OMe	56.31 *q*	56.30 *q*
Tyramines		
1″, 1‴	130.48, 130.41 *s*	131.04[b], 130.91[b] *s*
2″, 2‴	130.64, 130.52 *d*	130.47, 130.58 *d*
3″, 3‴	116.07, 116.93 *d*	116.04, 116.09 *d*
4″, 4‴	1156.70, 156.73 *s*	156.66[c], 156.68[c] *s*
5″, 5‴	116.07, 116.93 *d*	116.04, 116.09 *d*
6″, 6‴	130.64, 130.52 *d*	130.47, 130.58 *d*
7″, 7‴	35.45, 34.50 *t*	35.45[d], 35.50[d] *t*
8″, 8‴	42.11, 41.49 *t*	41.78, 42.07 *t*

[a] Multiplicity derived from DEPT and HMQC spectra.
[b–d] Assignments may be interchanged.

Since wound-induction in potato tuber discs had previously been demonstrated to generate hydroxycinnamic acid amides (Negrel et al., 1993) we undertook to determine whether cross-linked products such as those described above would also be a part of the mix. For this exercise potato wound periderm was prepared essentially as described by Negrel et al. (1996) and extracted in a manner similar to that for the scab lesions. Analysis by HPLC for hydroxycinnamic acid amides in the extracts consistently revealed a comparable measure of feruloyltyramines and feruloyloctopamines. However, cross-linked analogues such as compounds **5** and **6** though detectable were much reduced in comparison and constituted only a minor portion (<10%) of the total. The relative differences in cross-linked content detected might be attributable to the fact that scab lesion formation is an ongoing process while the tuber is under attack.

In summation four feruloylamides and two cross-linked feruloyltyramines associated with lesions of common scab infected potato tubers were isolated and fully characterized. Evidence for the presence of a minor complex of cross-linked dimers containing both feruloyltyramines and feruloyloctopamines was also demonstrated. To our knowledge this is the first report of such cross-linked compounds occurring in potato tubers. They are presumably formed by peroxide mediated reactions of feruloylamide monomers and may represent intermediates in formation of the polyphenol domains associated with the wound healing suberization process.

3. Experimental

3.1. General

All solvents used were HPLC grade. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates and Whatman $KC_{18}F$ plates. High-performance liquid chromatography (HPLC) studies utilized a Hewlett–Packard HPLC 1100 system and a Supercosil LC-18, 15 cm × 4.6 mm × 5 μm column eluted with water–acetonitrile–acetic acid (77:23:1) at a flow rate of 1.0 ml/min monitored at 325 nm with a Shimadzu SPD-M6A diode array UV–Vis detector.

Electrospray (ES) mass spectra (MS) were obtained on a Micromass Quattro Micro mass spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded for solutions in deuterated acetone on a Varian Unity 400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Chemical shifts were referenced to the solvent resonances (δ_H 2.05 ppm; and δ_C 29.80 ppm).

3.2. Isolation of hydroxycinnamic acid amide monomers and dimers

Field infected tubers (cv. Green Mountain) were washed with warm water. Lesion tissue (ca. 125 g per batch) was excised with a paring knife and homogenized with acetone (200 ml) in a Waring blender until a fine slurry was produced (ca. 45 s). The slurry was filtered under vacuum through Whatman No. 1 filter paper and the filter cake washed twice with 50 ml portions of acetone. The acetone in the combined filtrates was evaporated in vacuo at room temperature. The remaining aqueous residue was transferred to a separatory funnel and extracted with a 200 ml portion of $CHCl_3$. The $CHCl_3$ was removed in vacuo at room temperature and the yellow residue triturated three times with 10 ml portions of acetone. This solution was concentrated to ca. 5 ml, cooled in an ice bath and filtered to remove co-extracted waxes. The residue (145 mg) from this solution was fractionated by thin-layer chromatography on 1000 μm thickness Whatman $KC_{18}F$ plates with acetone–water (3:2) to furnish three major and one minor fraction that contained materials which exhibited a blue fluorescence when exposed to UV light. The major fractions averaged 10–12 mg each and the minor 2–3 mg. These crude fractions were further

purified by thin-layer chromatography on 200 μm thickness Whatman $KC_{18}F$ plates with acetone–water (3:2). The *cis* and *trans* isomers in each fraction were then separated on 250 μm thickness Whatman silica gel 60 A TLC plates with $CHCl_3$–MeOH (9:1) to yield essentially pure quantities of compounds **1–6** and a mixture of four cross-linked *trans* and *cis* hydroxycinnamic acid amide dimers containing both feruloyltyramine and feruloyloctopamine residues. Similar procedures were followed for the isolation of these compounds from non-scab lesion suberized potato material.

3.3. Compound characterization

N-trans-Feruloyloctopamine (**1**). Colourless oil; For ^{1}H NMR and ^{13}C NMR spectroscopic data, see Table 2. ES–MS $m/z = 330[M + H]^+$.

N-cis-Feruloyloctopamine (**2**). Colourless oil; For ^{1}H NMR and ^{13}C NMR spectroscopic data, see Table 2. ES–MS $m/z = 330[M + H]^+$.

N-trans-Feruloyltyramine (**3**). Colourless oil; ^{1}H NMR spectroscopic data δ 7.44 (1H, *d*, $J = 15.6$ Hz, H-7), 7.16 (1H, *d*, $J = 2.0$ Hz, H-2), 7.06 (2H, *d*, $J = 8.6$ Hz, H-2′, H-6′), 7.03 (1H, *dd*, $J = 8.0$, 2.0 Hz, H-6), 6.83 (1H, *d*, $J = 8.0$ Hz, H-5), 6.76 (2H, *d*, $J = 8.6$ Hz, H-3′, H-5′), 6.49 (1H, *d*, $J = 15.6$ Hz, H-8), 3.87 (3H, s, 4′-OMe), 3.47 (2 H, *m*, H-8′), 2.74 (2H, *t*, $J = 7.7$ Hz, H-7′). ES–MS $m/z = 314[M + H]^+$.

N-cis-Feruloyltyramine (**4**). Colourless oil; ^{1}H NMR spectroscopic data δ 7.88 (1H, br *s*, H-2), 7.11 (1 H, *dd*, $J = 8.2$, 2.0 Hz, H-6), 7.03 (2H, *d*, $J = 8.6$ Hz, H-2′, H-6′), 6.77 (1H, *d*, $J = 8.2$ Hz, H-5), 6.74 (2H, *d*, $J = 8.6$ Hz, H-3′, H-5′), 6.53 (1H, *d*, $J = 12.9$ Hz, H-7), 5.82 (1H, *d*, $J = 12.9$ Hz, H-8), 3.83 (3H, *s*, 4′-OMe), 3.42 (2 H, *m*, H-8′), 2.71 (2H, *t*, $J = 7.5$ Hz, H-7′). ES–MS $m/z = 314[M + H]^+$.

N-trans-Grossamide (**5**). Colourless oil; ^{1}H NMR spectroscopic data δ 7.41 (1H, *d*, $J = 15.7$ Hz, H-7), 7.09 (2H, *d*, $J = 8.4$ Hz, H-2‴, H-6‴), 7.09 (1H, *s*, H-2), 7.09 (2 H, *d*, $J = 8.3$ Hz, H-2″, H-6″), 6.99 (1 H, *s*, H-2′), 6.82 (1H, *s*, H-6′), 6.82 (1H, *s*, H-5′), 6.81 (2H, *d*, $J = 8.4$ Hz, H-3‴, H-5‴), 6.77 (2H, *d*, $J = 8.3$ Hz, H-3″, H-5″), 6.48, (1H, *d*, $J = 15.7$ Hz, H-8), 6.42 (1H, *s*, H-6), 6.03 (1H, *d*, $J = 8.5$ Hz, H-7′), 4.18 (1H, *d*, $J = 8.5$ Hz, H-8′), 3.85 (3H, *s*, 3-OMe), 3.82 (3H, *s*, 3′-OMe), 372 (1H, *m*, H-8a‴), 3.54 (2H, *m*, H-8″), 3.39 (1H, *m*, H-8b‴), 2.87 (1H, *m* H-7a‴), 2.79 (2H, *m*, H-7″), 2.74 (1H, *m*, H-7b‴). For ^{13}C NMR spectroscopic data, see Table 3. ES–MS *m/z* (rel. int.) = 625 (12) $[M + H]^+$, 488 (7) $[M - \text{tyramine} + H]^+$, 351 (66) $[M - 2 \times \text{tyramine} + H]^+$.

N-cis-Grossamide (**6**). Colourless oil; ^{1}H NMR spectroscopic data δ 7.61 (1H, br *s*, H-2), 7.10 (1H, br *s*, H-6), 7.02 (2H, *d*, $J = 8.5$ Hz, H-2‴, H-6‴), 7.00 (1H, br *s*, H-2′), 7.00 (2H, *d*,$J = 8.5$ Hz, H-2″, H-6″), 6.82 (1H, *s*, H-5′), 6.83 (1H, *s*, H-6′), 6.75 (2H, *d*, $J = 8.5$, H-3‴, H-5‴), 6.73 (2H, *d*, $J = 8.5$, H-3″, 5″), 6.57 (1H, *d*, $J = 12.8$, H-7), 5.99 (1H, *d*, $J = 7.8$, H-7′), 5.87 (1H, *d*, $J = 12.8$, H-8), 4.20 (1H, *s*, $J = 7.8$, H-8′), 3.84 (3H, *s*, 3-OMe), 3.82 (3H, *s*, 3′-OMe), 3.48 (2H, *m*, H-8‴), 3.44 (2H, *m*, H-8″), 2.76 (2H, *t*, $J = 7.3$, H-7″), 2.70 (2H, *t*, $J = 7.4$, H-7‴). For ^{13}C NMR spectroscopy data, see Table 3. ES–MS $m/z = 625$ $[M + H]^+$.

Hydroxycinnamic acid amide mixed dimers. Colourless oils; Pertinent ^{1}H NMR and ^{13}C NMR spectral data is outlined in the text. FAB-MS *m/z* (rel. int.) = 641 (9) $[M + H]^+$, 351 (100) $[M - \text{tyramine} - \text{octopamine} + H]^+$.

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