

Synthesis of naturally occurring cinnamyl cinnamates[†]

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A convenient, high yield and general method is described for the synthesis of cinnamyl cinnamates (**1a-f**, **2a-c** and **2e**) from benzaldehydes (**7a-f**). The aldehydes (**7a-f**) on reaction with phosphorane (**6**) provide the (*E,E*)-cinnamyl cinnamates (**1a-f**) in high yields together with the (*E,Z*)-esters (**2a-c** and **2e**) in low yields in the same reaction.

Keywords: cinnamyl cinnamates

Introduction

Propolis the material used by bees as glue, general purpose sealer and draught-excluder for beehives has been used for a long time for medicinal purposes.¹ Propolis is a complex mixture of organic substances. The presence of various cinnamyl cinnamates in propolis has been shown by the GC-MS technique.^{1,2} The phenolic esters from propolis have been identified^{1,2} as their trimethylsilyl ethers by comparing them by co-chromatography with authentic trimethylsilyl ethers prepared by using classical methods.¹

The cinnamyl cinnamates have been isolated in both *E,E*- and *E,Z*- forms from natural sources. Thus, the parent cinnamyl cinnamate (**1f**) has been isolated³ from the essential oil of the berries of *Lavungo scandens* (Roxb.) which is said to be of high medicinal value especially in curing baldness. The cinnamyl-(*E*)-cinnamates (**1a-d** and **1f**) have also been identified^{1,2,4} from the bud exudates of *Populus balsamifera* and other populus species. The structure of (*E*)-cinnamyl-(*E*)-cinnamate (**1f**) isolated from the male flower of *Alnus sieboldiana* has also been determined⁵ by spectral (IR, UV, ¹HNMR) and by chemical methods. (*E*)-Cinnamyl-(*Z*)-4-coumarate (**2a**) and (*E*)-cinnamyl-(*Z*)-isoferulate (**2b**) isolated^{4,6} from the bud exudates of *Populus nigra* and *Populus fremontii* have been identified as their trimethylsilyl derivatives by the GC-MS technique. The authors, however, could not confirm the structures of these compounds, by co-chromatography, with authentic samples because of the non-availability of (*Z*)-4-coumaric- and (*Z*)-isoferulic acids required for their synthesis.⁴ (*E*)-Cinnamyl (*E*)-cinnamates are valuable compounds as some of them possess termite attractant⁷ and lipoxygenase inhibitor⁸ activity. It is also reported⁹ that coniferyl ferulate might be an important compound for activating blood circulation and for removal of blood stasis. (*E*)-Cinnamyl-(*E*)-cinnamates are used⁷ in industry for the manufacturing of soaps, detergents, lotions and perfumes. (*E*)-Cinnamyl (*Z*)-cinnamates have been used as intermediates for the synthesis of lignans.¹⁰

A few methods are reported for the synthesis of (*E*)-cinnamyl-(*E*)-cinnamates. These methods^{10,11} involve reaction of cinnamoyl chloride with cinnamyl alcohol in the presence of base, or *in situ* reduction of carboxylic acids followed by esterification, using trimethylamine-borane^{11a} or involve palladium catalysed hydrocarboxylation^{11b} of allenes. All these methods provide (*E*)-cinnamyl-(*E*)-cinnamates. The method involving reduction of the triple bond of cinnamyl phenyl propiolate using Lindlar catalyst is reported for the synthesis of (*E*)-cinnamyl-(*Z*)-cinnamates.¹⁰ Although these methods are reported for the synthesis of cinnamyl cinnamates, apart from

1f none of the naturally occurring compounds (**1a-d**, **2a** and **2b**) have been synthesised in sizable amounts. Their physical and spectral properties are also not reported in the literature. These compounds have not been examined for their biological activity.

Results and discussion

As both (*E,E*- and *E,Z*-) cinnamyl cinnamates (**1a-d**, **1f** and **2a-b**) have been isolated from natural sources and the (*E,Z*)-isomers have high synthetic utility there was a need to develop a general and high yield method for the synthesis of these compounds. We report herein a convenient method for the synthesis of both (*E,E*) and (*E,Z*) esters. Our method (Scheme 1) involves the reaction of carbocinnamyloxymethylenetriphenylphosphorane (**6**) with benzaldehydes (**7a-f**). The phosphorane (**6**) required for this purpose was prepared from chloroester **5** which was prepared in 76% yield by reacting (*E*)-cinnamyl alcohol with chloroacetyl chloride in dichloromethane solution using pyridine as a base. The chloroester **5** on reaction with triphenylphosphine in benzene solution gave the phosphonium salt which on treatment with sodium hydroxide provided the phosphorane **6**.

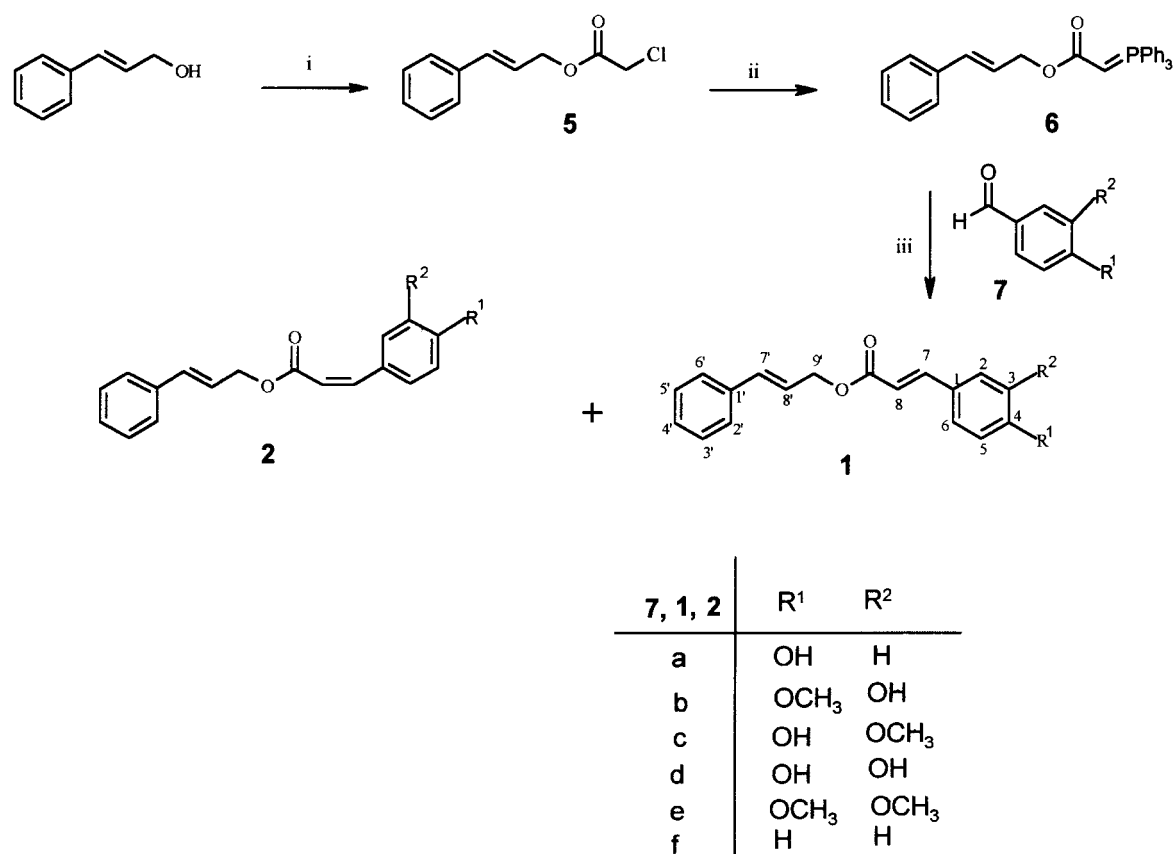
The phosphorane **6** on reaction with 4-hydroxybenzaldehyde (**7a**) in dichloromethane at room temperature provided (*E*)-cinnamyl-(*E*)-4-coumarate (**1a**), m.p. 106°C, in 74% yield and (*E*)-cinnamyl-(*Z*)-4-coumarate (**2a**), m.p. 125–126°C in 6% yield. Isovanillin (**7b**) on similar reaction with phosphorane **6** gave (*E*)-cinnamyl-(*E*)-isoferulate (**1b**) and its (*E,Z*)-isomer (**2b**) in 79 and 9% yield respectively. Reaction of phosphorane **6** with aldehydes (**7c** and **7e**) also gave the corresponding esters (**1c**, **1e**) and (**2c**, **2e**) in 73–87 and 2–15% yields. The aldehydes **7d** and **7f** on reaction with **6** provided exclusively the (*E*)-cinnamyl-(*E*)-cinnamates, **1d** (m.p. 159–160°C) and **1f** (m.p. 44–45°C, lit.⁵ 40–41°C) in 80 and 88% yields respectively.

The structures of all these compounds (**1a-f**) and (**2a-c** and **2e**) have been determined on the basis of their analytical and spectral properties. As (*E*)-cinnamyl alcohol was used for the preparation of phosphorane **6** the (*E*)-stereochemistry of the C₇–C₈ double bonds in products **1** and **2** was expected. The stereochemistry of the newly formed C₇–C₈ double bonds in **1** and **2** was determined by ¹HNMR spectroscopy. The (*E,E*) stereochemistry in **1a-f** and (*E,Z*) in (**2a-c** and **2e**) was clearly established from the coupling constants and chemical shifts of the olefinic protons. Thus, in the ¹HNMR spectrum of **1a** the H-7 and H-7' are seen as doublets (*J* 16.4 Hz) at 7.72 and 6.77 δ. The doublet and doublet of triplets of olefinic protons (H-8 and H-8') are merged in the signals of other protons. In the ¹HNMR spectrum of **2a** the H-7' is seen as doublet (*J* 16.2 Hz) and the H-7 and H-8 as doublets (*J* 12.6 Hz) at 6.92 and 5.90 δ respectively. The H-8' is seen as doublet of triplet (*J* 16.2 and 6.5 Hz) at 6.32 δ. Similar spectral properties were observed in other esters **1b-f** and **2b**, **2c** and **2e**. The ¹HNMR

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.



Scheme 1

Reagents and conditions: i) ClCH₂COCl, Pyridine, CH₂Cl₂ 0 °C ii) PPh₃/C₆H₆, rt, (NaOH) iii) CH₂Cl₂, rt, 2–3h.

properties exhibited by **1f** are identical⁵ with those reported for the natural product. These results establish the (*E,E*)- and (*E,Z*)- stereochemistry of compounds **1a–f** and **2a–c** and **2e** respectively.

In conclusion, a high yield method has been described in this paper for the synthesis of naturally occurring (*E*)-cinnamyl-(*E*)-cinnamates (**1a–d** and **1f**). The natural (*E*)-cinnamyl-(*Z*)-cinnamates (**2a** and **2b**) and the synthetic esters **2c** and **2e** have been obtained in low yields in this approach. The novelty of the present approach is that it requires milder reaction condition (neutral and at room temperature) and the final products are obtained in high yields.

Experimental

All melting points are uncorrected. All solid compounds were recrystallised from ethyl acetate-hexane. IR spectra of solids were recorded in nujol on Perkin-Elmer FT IR-1615 spectrometer. ¹H and ¹³C NMR spectra were recorded on Varian Mercury 300 MHz and Bruker AC-200 MHz spectrometers in CDCl₃ except **1d** which was recorded in DMSO-*d*₆. Chemical shifts are expressed in δ (ppm) downfield from Me₄Si and coupling constants in Hz. EI mass spectra were recorded on Finnigan Mat-1020 spectrometer with a direct inlet system. Elemental analyses were performed on a Hosli's rapid carbon-hydrogen analyser. Dichloromethane was distilled over CaH₂ and stored over molecular sieves. Silica gel (Achme, 100–200 mesh) was used for column chromatography.

(*E*)-Cinnamyl chloroacetate (**5**): A solution of (*E*)-cinnamyl alcohol (16 g, 119.4 mmol) dissolved in dichloromethane (110 ml) was cooled to 0 °C. Pyridine (14.5 ml, 179 mmol) was added to it and the mixture stirred for 10 min. Freshly distilled chloroacetyl chloride (10.5 ml, 132 mmol) was then added to it over a period of 10 min and the reaction mixture was stirred at 0 °C for 20 min. Water (20 ml) was added and the organic layer was separated out. The aqueous layer was extracted with dichloromethane (3 × 10 ml). The combined organic

layer was washed successively with 10 % HCl (5 × 100 ml), saturated NaHCO₃ solution and finally with water. The organic layer on drying (Na₂SO₄) and evaporation gave yellowish brown coloured liquid which was chromatographed over silica gel using hexane as solvent for elution to give ester **5** (19.1 g, 76%) as a colourless liquid (Found: C, 62.88; H, 5.43. Calc. for C₁₁H₁₁ClO₂: C, 62.70; H, 5.22%; ν_{max}/cm⁻¹ (Neat) 1755.5, 1654.1, 1167.0; δ_H (300 MHz), 4.11 (2H, s, -CH₂-Cl), 4.9 (2H, d, *J* 6.3 Hz, -CH₂-O-), 6.28 (1H, dt, *J* 15.6 and 6.3 Hz, Ar-CH=CH-), 6.69 (1H, d, *J* 15.6 Hz, Ar-CH=CH-), 7.26–7.43 (5H, m, Ar-H); δ_C (75 MHz), 40.8, 66.6, 121.8, 126.3, 128.1, 128.2, 135.1, 135.7, 166.9.

Carbocinnamylmethylenetriphenylphosphorane (**6**): Cinnamyl chloroacetate, **5** (19.1 g, 90.7 mmol) was added to a solution of triphenylphosphine (29.0 g, 110.6 mmol) in dry benzene (20 ml) and the reaction mixture was stirred at room temperature for 16h. The phosphonium salt thus obtained was filtered and washed with dry benzene. A solution of this salt in water (100 ml) and benzene (100 ml), containing a pinch of phenolphthalein was neutralised with aqueous sodium hydroxide till the pink colour persisted. The benzene layer was separated out and the aqueous layer extracted with benzene (2 × 25 ml). The combined benzene layer was dried (Na₂SO₄) and concentrated to about one fourth of its volume. Addition of hexane furnished the phosphorane (**6**, 17.20 g, 71%) as a crystalline solid; m.p. 133 °C; (Found: C, 79.43; H, 5.52. Calc. for C₂₉H₂₅O₂P: C, 79.81; H, 5.73%); *m/z* (EI): 436 (M⁺), 117.

General procedure for the preparation of cinnamyl cinnamates (**1a–f**, **2a–c** and **2e**): A solution of phosphorane, **6** (3.6 mmol) and appropriate aldehyde **7** (3 mmol) in dichloromethane (10 ml) was stirred at room temperature for 2–3 h (monitored by TLC). The solvent was removed under reduced pressure and the residue obtained was chromatographed over silica gel. For chromatographic purification of **1f** the eluent used was hexane, for **1d** ethyl acetate-hexane (2:8) and for the remaining compounds a gradient mixture of ethyl acetate-hexane (1:9) was used. The compounds **2a–c** and **2e** were obtained in initial fractions and **1a–f** in later fractions, as white solids, except **1c** which is a viscous liquid.

(*E*)-Cinnamyl-(*E*)-4-coumarate (**1a**): Yield 74%; m.p. 105–106°C; (Found: C, 77.10; H, 5.96. Calc. for C₁₈H₁₆O₃: C, 77.14; H, 5.71%), $\nu_{\max}/\text{cm}^{-1}$ 1747.4, 1690.1, 1626.8, 1603.0, 1165.3; δ_{H} (200 MHz), 4.90 (2H, d, *J* 6.5 Hz, CH₂), 5.50 (1H, bs, -OH), 6.31–6.47 (2H, m, H-8 and H-8'), 6.77 (1H, d, *J* 16.4 Hz, H-7'), 6.90 (2H, d, *J* 9.8 Hz, H-3 and H-5), 7.29–7.56 (7H, m, Ar-H), 7.72 (1H, d, *J* 16.4 Hz, H-7); δ_{C} (75 MHz), 65.3, 114.6, 115.9, 122.9, 126.6, 128.0, 128.5, 130.1, 134.3, 136.1, 145.5, 158.4, 167.9; *m/z* (EI): 280 (M+), 235, 186, 147, 117, 115, 107, 91, 77, 65.

(*E*)-Cinnamyl-(*E*)-isoferulate (**1b**): Yield 79%; m.p. 69–70°C; (Found: C, 73.27; H, 5.61. Calc. for C₁₉H₁₈O₄: C, 73.54; H, 5.80%), $\nu_{\max}/\text{cm}^{-1}$ 1688.5, 1628.8, 1610.9, 1160.3; δ_{H} (300 MHz), 3.92 (3H, s, OCH₃), 4.85 (2H, d, *J* 5.9 Hz, CH₂), 5.64 (1H, s, -OH), 6.23–6.41 (2H, m, H-8 and H-8'), 6.70 (1H, d, *J* 15.8 Hz, H-7'), 6.84 (1H, d, *J* 8.2 Hz, H-5), 7.02 (1H, bd, *J* 8.2 Hz, H-6), 7.13 (1H, s, H-2), 7.19–7.43 (5H, m, Ar-H), 7.60 (1H, d, *J* 16.4 Hz, H-7), δ_{C} (75 MHz), 55.9, 64.9, 110.5, 113.0, 115.7, 121.8, 123.3, 126.5, 127.8, 127.9, 128.5, 133.9, 136.1, 144.8, 145.8, 148.5, 166.9; *m/z* (EI): 310 (M+), 265, 226, 186, 177, 161, 145, 133, 124, 117, 115, 91, 77.

(*E*)-Cinnamyl-(*E*)-ferulate (**1c**): Yield 73%; Viscous liq., (Found: C, 73.77; H, 5.95. Calc. for C₁₉H₁₈O₄: C, 73.54; H, 5.80%), $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃), 1703.1, 1655.8, 1634.6, 1596.2, 1156.7, δ_{H} (200 MHz), 3.94 (3H, s, OCH₃), 4.88 (2H, d, *J* 7.0 Hz, CH₂), 5.94 (1H, bs, -OH), 6.30–6.47 (2H, m, H-8 and H-8'), 6.73 (1H, d, *J* 16.9 Hz, H-7'), 6.94 (1H, d, *J* 8.5 Hz, H-5), 7.08 (1H, bd, *J* 8.5 Hz, H-6), 7.14 (1H, bd, H-2), 7.29–7.47 (5H, m, Ar-H), 7.67 (1H, d, *J* 16.9 Hz, H-7), δ_{C} (75 MHz), 55.8, 64.9, 109.3, 114.7, 115.0, 123.0, 123.3, 126.5, 126.8, 127.9, 128.5, 134.0, 136.2, 145.1, 146.7, 147.9, 166.9; *m/z* (EI): 310 (M+), 265, 226, 161, 145, 117, 115, 91, 77, 65.

(*E*)-Cinnamyl-(*E*)-caffeate (**1d**): Yield 80%; m.p. 159–160°C (Found: C, 72.61; H, 5.13. Calc. for C₁₈H₁₆O₄: C, 72.97, H, 5.40%); $\nu_{\max}/\text{cm}^{-1}$ 1690.0, 1637.3, 1600.3, 1184.4; δ_{H} (200 MHz), 4.83 (2H, d, *J* 6.5 Hz, CH₂), 6.26 (1H, d, *J* 16.3 Hz, H-8), 6.35 (1H, partly resolved dt, *J* 16.3 and 6.5 Hz, H-8'), 6.70 (1H, d, *J* 16.3 Hz, H-7'), 6.75–6.89 (2H, m, H-5 and H-6), 7.06 (1H, bs, H-2), 7.23–7.46 (5H, m, Ar-H), 7.54 (1H, d, *J* 16.3 Hz, H-7), 9.14 (2H, bs, 2 × -OH); δ_{C} (75 MHz), 64.0, 113.4, 113.7, 114.9, 120.9, 122.8, 125.4, 125.7, 127.2, 127.8, 132.9, 135.9, 144.5, 144.8, 147.2, 166.2; *m/z* (EI): 296 (M+), 251, 180, 163, 117, 115, 105, 91, 77.

(*E*)-Cinnamyl-(*E*)-*O*,*O*-dimethyl caffeate (**1e**): Yield 87%; m.p. 99–101°C; (Found: C, 73.93; H, 6.01. Calc. for C₂₀H₂₀O₄: C, 74.07; H, 6.17%), $\nu_{\max}/\text{cm}^{-1}$ 1746.3, 1625.8, 1601.2, 1161.0; δ_{H} (300 MHz), 3.91 (6H, s, 2 × OCH₃), 4.85 (2H, d, *J* 6.7 Hz, CH₂), 6.34 (2H, m, H-8 and H-8'), 6.70 (1H, d, *J* 16.1 Hz, H-7'), 6.85 (1H, d, *J* 8.9 Hz, H-5), 7.02 (1H, bd, H-2), 7.10 (1H, bd, *J* 8.9 Hz, H-6), 7.17–7.40 (5H, m, Ar-H), 7.67 (1H, d, *J* 16.1 Hz, H-7); δ_{C} (75 MHz), 55.8, 64.9, 109.5, 110.8, 115.4, 122.4, 123.2, 126.4, 127.1, 127.8, 128.4, 133.9, 136.0, 144.7, 148.9, 150.9, 166.6; *m/z* (EI): 324 (M+), 240, 207, 191, 164, 117, 115, 105, 91, 77.

(*E*)-Cinnamyl-(*E*)-cinnamate (**1f**): Yield 88%; m.p. 44–45°C, (lit. 5 40–41°C) (Found: C, 82.02; H, 6.35. Calc. for C₁₈H₁₆O₂: C, 81.81; H, 6.06%); $\nu_{\max}/\text{cm}^{-1}$ 1712.9, 1636.9, 1575.9, 1161.9; δ_{H} (200 MHz), 4.90 (2H, d, *J* 6.7 Hz, CH₂), 6.36 (1H, dt, *J* 16.6 and 6.7 Hz, H-8'), 6.50 (1H, d, *J* 16.6 Hz, H-8), 6.73 (1H, d, *J* 16.6 Hz, H-7'), 7.23–7.26 (10H, m, Ar-H), 7.76 (1H, d, *J* 16.6 Hz, H-7), δ_{C} (75 MHz), 65.1, 117.8, 123.2, 126.5, 127.9, 128.5, 128.8, 130.2, 134.1, 134.2, 136.1, 144.9, 166.5; *m/z* (EI): 264 (M+), 219, 131, 117, 115, 103, 91, 77.

(*E*)-Cinnamyl-(*Z*)-4-coumarate (**2a**): Yield 6%; m.p. 125–126°C (Found: C, 76.91; H, 5.56. Calc. for C₁₈H₁₆O₃: C, 77.14; H, 5.71%); $\nu_{\max}/\text{cm}^{-1}$ 1747.2, 1689.6, 1599.3, 1166.2; δ_{H} (300 MHz), 4.82 (2H, dd, *J* 6.5 and 2.0 Hz, CH₂), 5.35 (1H, bs, -OH), 5.90 (1H, d, *J* 12.6 Hz, H-8), 6.32 (1H, dt, *J* 16.2 and 6.5 Hz, H-8'), 6.70 (1H, d, *J* 16.2 Hz, H-7'), 6.82 (2H, d, *J* 9.7 Hz, H-3 and H-5), 6.92 (1H, d, *J* 12.6 Hz, H-7), 7.25–7.45 (7H, m, Ar-H), 7.67 (2H, d, *J* 9.7 Hz, H-2 and H-6); δ_{C} (75 MHz), 65.0, 115.0, 116.5, 122.9, 126.5, 127.0, 127.9,

128.5, 132.2, 134.2, 136.0, 144.2, 156.8, 166.5; *m/z* (EI): 280 (M+), 251, 235, 186, 147, 117, 115, 91, 77.

(*E*)-Cinnamyl-(*Z*)-isoferulate (**2b**): Yield 9%; m.p. 72–73°C (Found: C, 73.23; H, 5.53. Calc. for C₁₉H₁₈O₄: C, 73.54; H, 5.80%); $\nu_{\max}/\text{cm}^{-1}$ 1707.7, 1609.0, 1576.8, 1172.8; δ_{H} (300 MHz), 3.89 (3H, s, OCH₃), 4.81 (2H, dd, *J* 6.9 and 2.0 Hz, CH₂), 5.88 (1H, d, *J* 13.6 Hz, H-8), 6.31 (1H, dt, *J* 17.0 and 6.9 Hz, H-8'), 6.55 (1H, bd, *J* 17.0 Hz, H-7'), 6.81 (1H, d, *J* 8.5 Hz, H-5), 6.88 (1H, d, *J* 13.6 Hz, H-7), 7.22–7.43 (8H, m, Ar-H); δ_{C} (75 MHz), 55.8, 64.8, 109.8, 116.2, 117.4, 123.0, 126.5, 127.8, 128.0, 128.4, 133.9, 136.1, 143.2, 144.8, 147.3, 165.9; *m/z* (EI): 310 (M+), 265, 226, 177, 161, 150, 133, 117, 115, 105, 91, 77.

(*E*)-Cinnamyl-(*Z*)-ferulate (**2c**): Yield 15%; m.p. 75–77°C (Found: C, 73.33; H, 5.93. Calc. for C₁₉H₁₈O₄: C, 73.54; H, 5.80%); $\nu_{\max}/\text{cm}^{-1}$ 1712.0, 1658.6, 1618.4, 1164.6; δ_{H} (300 MHz), 3.85 (3H, s, OCH₃), 4.79 (2H, d, *J* 5.9 Hz, CH₂), 5.84 (1H, s, -OH), 5.85 (1H, d, *J* 12.9 Hz, H-8), 6.30 (1H, dt, *J* 15.8 and 6.4 Hz, H-8'), 6.65 (1H, d, *J* 16.4 Hz, H-7'), 6.83 (1H, d, *J* 12.9 Hz, H-7), 6.87 (1H, d, *J* 8.2 Hz, H-5), 7.14 (1H, bd, *J* 8.2 and 1.7 Hz, H-6), 7.2–7.35 (5H, m, Ar-H); 7.76 (1H, d, *J* 1.7 Hz, H-2), δ_{C} (75 MHz), 55.9, 64.8, 112.7, 113.8, 116.3, 123.2, 125.6, 126.5, 127.0, 127.9, 128.5, 133.9, 136.1, 144.1, 145.7, 146.9, 166.0; *m/z* (EI): 310 (M+), 265, 226, 177, 161, 145, 133, 124, 117, 115, 105, 91, 77.

(*E*)-Cinnamyl-(*Z*)-*O*,*O*-dimethyl caffeate (**2e**): Yield 2%; m.p. 81–83°C (Found: C, 73.79; H, 6.04. Calc. for C₂₀H₂₀O₄: C, 74.07; H, 6.17%); $\nu_{\max}/\text{cm}^{-1}$ 1701.6, 1618.0, 1595.1, 1162.4; δ_{H} (300 MHz), 3.89 (6H, s, 2 × OCH₃), 4.80 (2H, d, *J* 6.4 Hz, CH₂), 5.88 (1H, d, *J* 12.9 Hz, H-8), 6.32 (1H, dt, *J* 15.2 and 6.7 Hz, H-8'), 6.68 (1H, d, *J* 15.2 Hz, H-7'), 6.78–6.89 (2H, t, Ar-H), 7.20–7.41 (6H, m, Ar-H), 7.67 (1H, bs, H-2); δ_{C} (75 MHz), 55.8, 55.8, 64.7, 110.3, 113.2, 116.8, 123.2, 124.7, 126.5, 127.5, 127.9, 128.5, 136.2, 143.8, 148.2, 150.1, 166.1; *m/z* (EI): 324 (M+), 240, 207, 176, 164, 148, 133, 117, 115, 105, 91, 77.

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