Dimethyldioxirane Oxidation of (*E,E*)-Cinnamylideneacetophenones

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The (*E,E*)-cinnamylideneacetophenones **1a–f** were oxidised by isolated dimethyldioxirane (DMD, as acetone solution) at room temperature, giving diastereomeric mixtures of the α,β:γ,δ-diepoxides **3a–f** when an excess of oxidant was used. α,β-Monoepoxides, found as minor components of the reaction, could be detected in only two cases (**2c,d**) when one equivalent of DMD was used. Dimethyldioxirane oxidation of (*E,E*)-2′-hydroxycinnamylideneacetophenones (**4a–d**) led to the formation of diastereomeric mixtures of the α,β:γ,δ-diepoxides **6a–d** as well as to the γ,δ-monoepoxides **5a–d** as minor products. The diepoxides **6a–d** were transformed into the isolable coumaranone derivatives **7a–d** during their chromatographic purification. All the compounds described have been fully characterised by NMR spectroscopy.

Introduction

(*E,E*)-Cinnamylideneacetophenones are well-known unsaturated ketones. The first synthesis of their parent compound 1,5-diphenylpenta-2,4-dien-1-one (**1a**) was reported as early as 1895.[1] Since then the synthesis and chemical transformations of a wide variety of substituted derivatives have been described in the literature. However, their epoxidation has hitherto received less attention. The α,β-monoepoxide of 1,5-diphenylpenta-2,4-dien-1-one was first prepared by Weitz and Scheffer in l921.[2] An asymmetric synthesis of the α,β-monoepoxides of (*E,E*)-cinnamylideneacetophenones and related unsaturated ketones was performed by Juliá's enantioselective epoxidation.[3] However, these experiments can only be considered as sporadic attempts to study the epoxidation of such unsaturated ketones.

2′-Hydroxycinnamylideneacetophenones [5-aryl-1-(2-hydroxyphenyl)penta-2,4-dien-1-ones] are important intermediates in the synthesis of biologically active compounds, and some of their oxidative transformations have already been investigated in detail. Probably the first example for the oxidative conversion of 2′-hydroxycinnamylideneacetophenones into 2-styrylchromones and 3-hydroxy-2-styrylchromones by treatment with selenium dioxide and alkaline hydrogen peroxide, respectively, was reported by Marini-Bettolo.[4] Recently, we have studied the oxidative cyclisation of 2′-hydroxycinnamylideneacetophenones with dimethyl sulfoxide in the presence of a catalytic amount of iodine, and new procedures have been developed for the synthesis of 2-styrylchromone derivatives.[5] We have also developed a new method for the synthesis of 3-styrylchromones by the oxidative transformation of 2′-hydroxycinnamylideneacetophenones with thallium(III) trinitrate.[6] Although various oxidative transformations of these unsaturated ketones have already been performed, to the best of our knowledge their epoxidation has not yet been published in the literature.

All these facts prompted us to investigate the epoxidation of (*E,E*)-cinnamylideneacetophenones as well as their 2′-hydroxy derivatives. On the basis of its successful utilisation for the epoxidation of a wide variety of unsaturated compounds, dimethyldioxirane appeared to be a convenient reagent for this purpose. This highly effective oxidant was advantageously used even in the case of electron-deficient olefins, such as chalcones and related α,β-unsaturated ketones,[7] or for the stereoselective epoxidation of exocyclic α,β-enones.[8] Since the dimethyldioxirane acts under strictly neutral conditions, it proved to be the best reagent for the epoxidation of 2′-hydroxychalcones[9] because these epoxides are extremely unstable under both acidic and basic conditions. As a result, the preparation of such epoxides was impossible with any other oxidant. Dimethyldioxirane and methyl(trifluoromethyl)dioxirane have been used successfully for the regioselective epoxidation of dienes and trienes as well.[10] Herein we report the dimethyldioxirane oxidation of (*E,E*)-cinnamylideneacetophenones and their 2′-hydroxy derivatives.

Results and Discussion

Epoxidation Experiments

Since the cinnamylideneacetophenones have two double bonds to be epoxidised, one of our aims was to investigate the regioselectivity of their epoxidation with dimethyldioxirane. For this purpose, compounds **1a−f** were allowed to react with one equivalent of isolated dimethyldioxirane in acetone (0.05−0.10 M) at room temperature; a multicomponent crude reaction product was obtained in each case.

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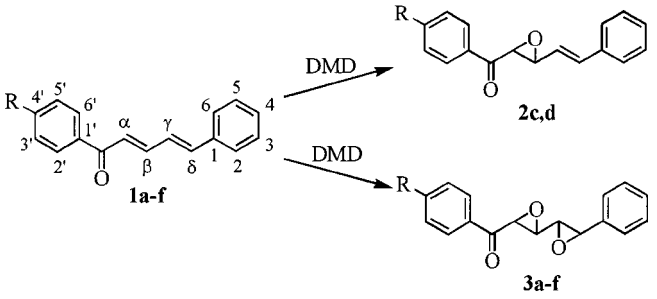
In these mixtures a substantial amount of starting material, α,β:γ,δ-diepoxides and several minor components were detected by thin-layer chromatography. The starting materials **1a−f** and the α,β:γ,δ-diepoxides **3a−f** were separated from the mixtures by preparative thin-layer chromatography. The α,β-monoepoxide could be observed and characterised by NMR spectroscopy of these mixtures in only two cases (**2c,d**, Scheme 1). However, the isolation of these α,β-monoepoxides was not possible in any case, even after a careful chromatographic analysis.



a) R = H; b) R = Me; c) R = OMe; d) R = F; e) R = Cl; f) R = Br

Scheme 1

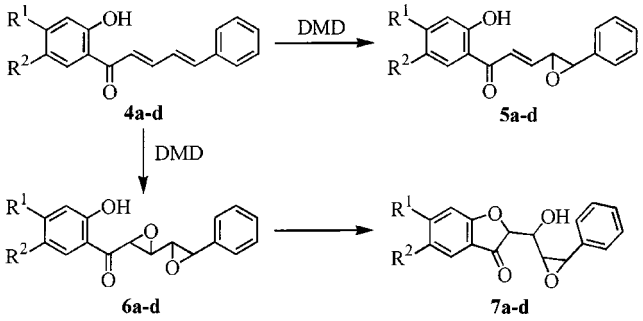
The α,β-double bond was epoxidised regioselectively by other oxidising agents (vide supra)[2,3] which means that it is more reactive towards a nucleophilic oxidant than the γ,δ-bond. However, this regioselectivity seems to be much less pronounced in the case of an electrophilic oxidant like dimethyldioxirane. For this reason, the α,β:γ,δ-diepoxide is the major oxidised product even when using only one equivalent of dimethyldioxirane; the appropriate α,β-monoepoxide is only a minor component in the reaction mixture and could not be isolated in every case. The α,β-monoepoxides **2c,d** were characterised by ^{1}H and ^{13}C NMR spectroscopy.

The complete conversion of the (*E,E*)-cinnamylideneacetophenones **1a−f** required four equivalents of dimethyldioxirane to afford the α,β:γ,δ-diepoxides **3a−f** (Scheme 1 and Table 1). No minor component could be isolated after column chromatography, and compounds **3a−f** were the only isolable products. On this basis it appears that there is a minimum regioselectivity between the two double bonds towards this electrophilic oxidant. ^{1}H and ^{13}C NMR measurements (vide infra) revealed that approximately 2:1 mixtures of diastereomeric α,β:γ,δ-diepoxides were formed in all cases. Separation of the two diastereomeric α,β:γ,δ-diepoxides was not possible.

Epoxidation of the (*E,E*)-2′-hydroxycinnamylideneacetophenones **4a−d** by dimethyldioxirane seemed to be an especially interesting challenge since this oxidant has been shown to be the reagent of choice for an effective preparation of the epoxides of 2′-hydroxychalcones.[9] For this reason, compounds **4a−d** were allowed to react with 3−5 equivalents of dimethyldioxirane, at ambient temperature, for 72−120 h, to give a complete conversion of the starting 2′-hydroxycinnamylideneacetophenones (Scheme 2). As a result, a multicomponent mixture was obtained in each case. An NMR analysis of these reaction mixtures allowed the characterisation of the γ,δ-monoepoxides **5a−d** and the diastereomeric mixtures of α,β:γ,δ-diepoxides **6a−d**. However, a preparative silica gel thin-layer chromatographic analysis of these mixtures led to the isolation of the γ,δ-monoepoxides **5a−d** and the new compounds **7a−d**; the α,β:γ,δ-diepoxides **6a−d** were not detected (Scheme 2). The coumaranone derivatives **7a−d** were obtained by cyclisation of the α,β:γ,δ-diepoxides **6a−d** on silica gel, probably due to the acidic character of the silica gel. This behaviour is in accordance with our previous observations on the epoxidations of 2′-hydroxyacrylophenone and 1-(2-hydroxyphenyl)-2-alken-1-ones, where the labile epoxides cyclised spontaneously giving the analogous 2-(α-hydroxyalkyl)-3-coumaranones.[9] The coumaranone derivatives **7a−d** were also obtained as diastereomeric mixtures (Scheme 2).

Table 1. Diastereomeric mixtures of α,β,γ,δ-Diepoxides **3a−d**

Compound (yellow oil)	Molecular formula	Yield (%)	Component (%) Major	Minor
3a	$C_{17}H_{14}O_3$	60	65	35
3b	$C_{18}H_{16}O_3$	62	64	36
3c	$C_{18}H_{16}O_4$	55	65	35
3d	$C_{17}H_{13}FO_3$	60	67	33
3e	$C_{17}H_{13}ClO_3$	63	68	32
3f	$C_{17}H_{13}BrO_3$	59	68	32



a) $R^1 = R^2 = H$; b) R^1 = Me, R^2 = H; c) R^1 = H, R^2 = F; d) R^1 = H, R^2 = Cl

Scheme 2

Contrary to compounds **1a−f**, the dimethyldioxirane oxidation of the (*E,E*)-2′-hydroxycinnamylideneacetophenones **4a−d** led to the isolation of the γ,δ-monoepoxides **5a−d** (Scheme 2) by preparative thin-layer chromatography. The formation of such monoepoxides might be envisaged in two ways: i) the formation of coumaranone-type compounds by the attack of the 2-hydroxy group at the β-carbon, leaving only the γ,δ-double bond available for epoxidation, or ii) the intramolecular hydrogen bond between the 2′-hydroxy and the carbonyl groups may enhance the reactivity of the γ,δ-double bond towards the dimethyldioxirane. The first hypothesis was ruled out since we followed the epoxidation reaction of **4a** by NMR spectroscopy and no coumaranone was observed: only the γ,δ-monoepoxide **5a** and the α,β:γ,δ-diepoxide **6a** were formed; no α,β-monoepoxide could be observed. The epoxidation of 2′-

acetoxycinnamylideneacetophenone lead to the formation of the corresponding α,β:γ,δ-diepoxide and to the α,β-monoepoxide as minor product, as in the case of compounds **1a−f** without the 2′-hydroxy group, thus confirming that the intramolecular hydrogen bond mentioned previously enhances the reactivity of the γ,δ-double bond towards the dimethyldioxirane.

NMR Spectroscopy

The aliphatic region of the ^{1}H NMR spectra of the isolated compounds **3a−f** presents two groups of four signals (δ = 4.27−4.33, 3.30−3.35, 3.15−3.18, 3.87−3.92 and δ = 4.29−4.33, 3.38−3.46, 3.23−3.28, 3.89−3.95), which were assigned to two spin systems by the analysis of their COSY spectra. These signals were attributed to the resonances of H-α, H-β, H-γ and H-δ of a diastereomeric mixture of the α,β:γ,δ-diepoxides **3a−f**, in a ratio of approximately 2:1. The carbon resonances of C-α, C-β, C-γ and C-δ of these diastereomers **3a−f** were assigned based on the correlations found in their HSQC (δ = 54.2−54.7, 57.2−57.7, 59.3−59.7, 56.7−57.6 and δ = 53.7−54.2, 56.2−56.4, 58.5−58.8, 55.8−56.3, respectively). The assignments of H-α (δ = 4.27−4.33 and 4.29−4.33) were confirmed by the connectivities found in the HMBC spectra with the carbonyl carbon resonances (δ = 191.2−192.9), whereas those of H-δ (δ = 3.87−3.92 and 3.89−3.95) show connectivities with the carbon resonances of C-1 (δ = 135.3−135.7) and C-2,6 (δ = 125.4−125.7). The analysis of the NOESY spectra of **3a−f** did not allow us to determine the stereochemistry of these diastereomers.

In the ^{1}H NMR spectra of the mixtures obtained in the reactions of **1c,d** with one equivalent of dimethyldioxirane it was possible to identify the proton resonances of the diastereomeric mixtures of diepoxides **3c,d** and also four other resonances at δ = 4.26−4.27, 3.73−3.74, 6.03 and 6.88−6.90 could be observed. In the HSQC spectra of such mixtures, these resonances correlate with the carbon signals at δ = 59.0−59.3, 59.6−59.8, 124.2−124.4 and 136.2−136.7, respectively, and their COSY spectra revealed that they belong to only one spin system. These results suggest the presence of monoepoxides of compounds **1c,d**. The unequivocal assignment of the structures of these monoepoxides **2c,d** was based on the connectivities found in the HMBC spectra of these reaction mixtures. The proton resonances at δ = 3.73−3.74 and 6.03 correlate with those of C=O (δ = 191.4−191.8) and C-1 (δ = 135.7−135.8), respectively, and were assigned to H-β and H-γ, respectively, thus confirming the presence of the α,β-monoepoxides **2c,d** (Scheme 1).

The ^{1}H NMR spectra of the mixtures obtained from the reaction of the 2′-hydroxycinnamylideneacetophenones **4a−d** with an excess (3−5 equivalents) of dimethyldioxirane show three hydroxylic proton resonances at δ = 11.52−11.80, 11.55−11.85 and 12.29−12.62. The latter was assigned to the 2′-OH of the monoepoxides **5a−d**, as was proved (vide infra) after their isolation by thin-layer chromatography. The presence of the other two hydroxylic resonances and the analysis of the aliphatic region of the ^{1}H NMR spectra of the reaction mixtures suggest the formation of a diastereomeric mixture of the α,β:γ,δ-diepoxides **6a−d** of the 2′-hydroxycinnamylideneacetophenones **4a−d**. The COSY spectra of these mixtures revealed the presence of two spin systems (δ = 4.29−4.40, 3.39−3.43, 3.19−3.21, 3.91−3.94 and δ = 4.31−4.42, 3.49−3.53, 3.28−3.31, 3.94−3.98), which were assigned to the resonances of H-α/H-β and H-γ/H-δ of the two diastereomers of the diepoxides **6a−d**, respectively. The assignment of H-α and H-δ was confirmed by the connectivities found in the HMBC spectra of these mixtures (Figure 1), the former with the carbonyl carbon (C=O) and the latter with the C-1 and C-2,6 carbon atoms. Other important connectivities found in these HMBC spectra are those of the hydroxylic proton (2′-OH) with C-1′, C-2′ and C-3′, and also those of H-6′ with C-2′, C-4′ and C=O, which allowed the assignment of these carbon resonances and support the structure of the diastereomers of the α,β:γ,δ-diepoxides **6a−d**. The assignments of the majority of the protonated carbon resonances of these two diastereomeric diepoxides **6a−d** were made by the analysis of the HSQC spectra of the referred reaction mixtures.

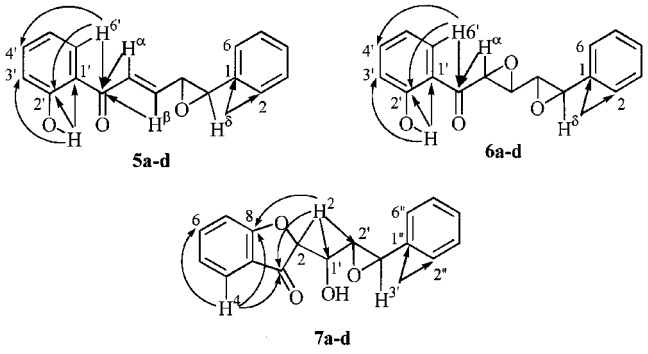


Figure 1. Main connectivities found in the HMBC spectra of compounds **5a−d, 6a−d** and **7a−d**

By careful thin-layer chromatographic analysis of the reaction mixtures of the 2′-hydroxycinnamylideneacetophenones **4a−d** with dimethyldioxirane two sets of compounds were isolated, one being the monoepoxides **5a−d** and the other being compounds **7a−d** (Scheme 2); the α,β:γ,δ-diepoxides **6a−d** were not detected.

The main characteristics of the ^{1}H NMR spectra of compounds **5a−d** were the proton resonances at δ = 7.32−7.40, 7.06−7.13, 3.62−3.65, 3.90−3.91 and 12.29−12.62, the latter being assigned to the 2′-OH proton. These data and the corresponding carbon resonances (δ = 124.1−125.3, 144.2−147.7, 60.9−61.1 and 61.8−62.0), assigned with the aid of the HSQC spectra, suggest the presence of a monoepoxide in each case. However, the correlations observed in the HMBC spectra of **5a−d** (Figure 1) between the proton resonances at δ = 7.32−7.40 and 7.06−7.13 and those of the carbonyl carbons, allowed us to assign these proton resonances to H-α and H-β, respectively, and to unequivocally prove the structure of the γ,δ-monoepoxides **5a−d** (Scheme 2). Other important correlations observed in the

HMBC spectra of **5a−d** are those of H-δ (δ = 3.90−3.91) with C-1 and C-2,6 and also those of the hydroxylic proton with C-1′, C-2′ and C-3′, which supports the structure of the γ,δ-monoepoxides **5a−d**.

The analysis of the aliphatic region of the ^{1}H NMR spectra of compounds **7a−d** with the aid of the COSY spectra allowed the assignment of four signals of two spin systems (δ = 4.73−4.79, 4.39−4.45, 3.36−3.38, 3.99−4.08 and δ = 4.76−4.82, 4.39−4.45, 3.24−3.25, 3.96−4.10). These proton resonances correlate in the HSQC spectra with those of the carbons at δ = 84.4−85.5, 69.5−69.6, 61.3−61.5, 56.0−56.4 and δ = 84.4−85.6, 69.8−69.9, 60.0−60.4, 55.4−55.8, respectively. All these data suggest that the α,β:γ,δ-diepoxides **6a−d** were transformed into new compounds during the thin-layer chromatographic purification. These new compounds retain one oxirane ring while the other epoxide has reacted with the 2′-hydroxy group. The connectivities found in the HMBC spectra of **7a−d** between the protons of each methynic group (H-2, δ = 4.73−4.79 and 4.76−4.82) with the carbonyl groups (C-3), with the strongly deshielded quaternary carbon (C-8), with the carbon of the epoxide ring (C-2′) and with another methynic carbon (C-1′) led us to suppose the formation of a coumaranone-type structure by oxirane ring opening at the α-position (**7a−d**, Scheme 2). Other important connectivities are those of H-4 with C-3, C-6 and C-8 and also of H-3′ with C-1′′ and C-2′′,6′′ (Figure 1), which allowed us to assign these carbon resonances and support the structures shown for compounds **7a−d**.

Experimental Section

General Remarks: Melting points (uncorrected): Reichert Thermovar apparatus fitted with a microscope. − FT NMR: Bruker DRX 300 spectrometer (300.13 and 75.47 MHz, for ^{1}H and ^{13}C, respectively); $CDCl_3$ as solvent, TMS as internal reference, chemical shifts (δ) in ppm, coupling constants (*J*) in Hertz (Hz). Unequivocal ^{1}H assignments were made with the aid of 2D-COSY (^{1}H/^{1}H) and NOESY spectra (phase sensitive experiment, mixing time of 800 ms), while ^{13}C assignments were made on the basis of 2D-HSQC (^{1}H/^{13}C, delay for the one bond *J* C/H couplings was optimised at 147 Hz) and HMBC (delays for one bond and long-range *J* C/H couplings were optimised at 147 and 7 Hz, respectively) experiments. All the 2D spectra were acquired using the standard Bruker microprograms. Elemental Analysis: Microanalytical laboratory of the Department of Organic Chemistry, University of Debrecen. − Preparative thin-layer chromatography: Merck or Riedel silica gel 60 DGF_{254}. − Column chromatography: Merck silica gel 60 with hexane/acetone (7:3 v/v) as eluent. Starting materials **1a−f** and **4a,d** were synthesised according to known procedures.[1,11−16] Dimethyldioxirane (as an acetone solution) was prepared as described[17] and its peroxide content was determined iodometrically.

(*E*,*E*)-2′-Hydroxy-4′-methylcinnamylideneacetophenone (4b): A 60% aqueous solution of sodium hydroxide (160 mL) was added to a methanolic solution (160 mL) of 2′-hydroxy-4′-methylacetophenone (4.0 mL, 30 mmol). This solution was allowed to cool to room temperature and cinnamaldehyde (5.0 mL, 35 mmol) was then added. The reaction mixture was stirred at room temperature for 20 h, then poured onto crushed ice and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water and recrystallised from methanol to obtain 6.4 g of **4b** (80%) as yellow crystals, m.p. 138−139 °C. ^{1}H NMR: δ = 2.36 (s, 3 H, CH_3), 6.73 (br. d, *J* = 8.1 Hz, 1 H, H-5′), 6.82 (br. s, 1 H, H-3′), 6.98−7.12 (m, 2 H, H-γ,δ), 7.19 (d, *J* = 14.7 Hz, 1 H, H-α), 7.31−7.41 (m, 3 H, H-3,4,5), 7.51 (d, *J* = 6.7 Hz, 1 H, H-2,6), 7.64−7.73 (m, 1 H, H-β), 7.72 (d, *J* = 8.1 Hz, 1 H, H-6′), 12.98 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 22.0 (CH_3), 117.8 (C-1′), 118.6 (C-3′), 120.1 (C-α), 126.7 (C-γ), 127.4 (C-2,6), 128.9 (C-3,5), 129.38 and 129.41 (C-4 and C-6′), 136.0 (C-1), 142.6 (C-δ), 145.0 (C-β), 148.0 (C-4′), 163.7 (C-2′), 193.1 (C=O). − $C_{18}H_{16}O_2$ (264.3): calcd. C 81.79, H 6.10; found C 81.72, H 6.12.

(*E*,*E*)-5′-Fluoro-2′-hydroxycinnamylideneacetophenone (4c): According to the procedure described for **4b**, 5′-fluoro-2′-hydroxyacetophenone (4.6 g, 30 mmol) afforded **4c** (6.1 g, 76%) as yellow crystals, m.p. 159−160 °C. ^{1}H NMR: δ = 6.98 (dd, $J_{H\text{-}F}$ = 4.6 and $J_{H\text{-}H}$ = 8.8 Hz, 1 H, H-3′), 7.04−7.13 (m, 2 H, H-γ,δ), 7.10 (d, *J* = 14.9 Hz, 1 H, H-α), 7.23 (dt, $J_{H\text{-}F}$ = 8.8 and $J_{H\text{-}H}$ = 2.9 and 8.8 Hz, 1 H, H-4′), 7.33−7.42 (m, 3 H, H-3,4,5), 7.51 (dd, $J_{H\text{-}F}$ = 8.8 and $J_{H\text{-}H}$ = 2.9 Hz, 1 H, H-6′), 7.52−7.54 (m, 2 H, H-2,6), 7.74 (ddd, *J* = 1.5, 8.0 and 14.9 Hz, 1 H, H-β), 12.64 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 114.4 (d, $J_{C\text{-}F}$ = 23.3 Hz, C-3′), 119.4 (d, $J_{C\text{-}F}$ = 6.0 Hz, C-1′), 119.7 (d, $J_{C\text{-}F}$ = 7.2 Hz, C-3′), 122.8 (C-α), 123.7 (d, $J_{C\text{-}F}$ = 23.5 Hz, C-4′), 126.4 (C-γ), 127.5 (C-2,6), 128.9 (C-3,5), 129.7 (C-4), 135.7 (C-1), 143.6 (C-δ), 146.3 (C-β), 154.8 (d, $J_{C\text{-}F}$ = 238.2 Hz, C-5′), 159.6 (C-2′), 192.7 (d, $J_{C\text{-}F}$ = 2.5 Hz, C=O). − $C_{17}H_{13}FO_2$ (268.3): calcd. C 76.11, H 4.88; found C 76.07, H 4.85.

General Procedure for the Preparation of the α,β:γ,δ-Diepoxides 3a−f of the (*E*,*E*)-Cinnamylideneacetophenones 1a−f: The required amount of isolated dimethyldioxirane in acetone (0.05−0.10 M) was added to a solution of the appropriate (*E,E*)-cinnamylideneacetophenone (**1a−f**; 1.17−1.57 g, 5.0 mmol) in anhydrous dichloromethane (20 mL) at room temperature. The mixture was left to stand at room temperature and another equivalent of dimethyldioxirane was added every day until the complete consumption of the starting material **1a−f**. A complete conversion of the starting materials into the appropriate α,β:γ,δ-diepoxides was achieved by using four equivalents of dimethyldioxirane in 96 h. The solvent was then evaporated under reduced pressure (ca. 20 Torr) and the residue was purified by column chromatography [hexane/acetone (7:3 v/v) as eluent] to yield the diepoxides **3a−f** (Scheme 1 and Table 1).

Diastereomeric Mixture (35:65) of α,β:γ,δ-Diepoxycinnamylideneacetophenone (3a)

Major Isomer: ^{1}H NMR: δ = 3.15 (dd, *J* = 1.9 and 4.5 Hz, 1 H, H-γ), 3.30 (dd, *J* = 1.9 and 4.5 Hz, 1 H, H-β), 3.87 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.33 (d, *J* = 1.9 Hz, 1 H, H-α), 7.21−7.32 (m, 5 H, H-2,3,4,5,6), 7.41−7.47 (m, 2 H, H-3′,5′), 7.57 (t, *J* = 7.5 Hz, 1 H, H-4′), 7.99 (d, *J* = 7.6 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.2 (C-α), 56.7 (C-δ), 57.3 (C-β), 59.3 (C-γ), 125.38 (C-2,6), 128.03 (C-2′,6′), 128.26 (C-3,4,5), 128.6 (C-3′,5′), 133.8 (C-4′), 134.9 (C-1′), 135.3 (C-1), 192.8 (C=O).

Minor Isomer: ^{1}H NMR: δ = 3.23 (dd, *J* = 2.0 and 3.2 Hz, 1 H, H-γ), 3.38 (dd, *J* = 2.0 and 3.2 Hz, 1 H, H-β), 3.89 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.33 (d, *J* = 2.0 Hz, 1 H, H-α), 7.21−7.32 (m, 5 H, H-2,3,4,5,6), 7.41−7.47 (m, 2 H, H-3′,5′), 7.57 (t, *J* = 7.5 Hz, 1 H, H-4′), 7.99 (d, *J* = 7.6 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 53.7 (C-α), 55.8 (C-δ), 56.3 (C-β), 58.5 (C-γ), 125.40 (C-2,6), 128.06 (C-2′,6′), 128.30 (C-4), 128.34 (C-3,5), 128.6 (C-3′,5′), 133.8 (C-4′), 134.9 (C-1′), 135.5 (C-1), 192.9 (C=O).

Diastereomeric Mixture (36:64) of 4′-Methyl-α,β:γ,δ-diepoxycinnamylideneacetophenone (3b)
Major Isomer: ^{1}H NMR: δ = 2.42 (s, 3 H, CH_3), 3.17 (dd, *J* = 2.0 and 4.6 Hz, 1 H, H-γ), 3.33 (dd, *J* = 2.0 and 4.6 Hz, 1 H, H-β), 3.90 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.32 (d, *J* = 2.0 Hz, 1 H, H-α), 7.25−7.35 (m, 7 H, H-2,3,3′,4,5,5′,6), 7.94 (d, *J* = 8.3 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 21.7 (*C*H_3), 54.4 (C-α), 57.0 (C-δ), 57.5 (C-β), 59.7 (C-γ), 125.55 (C-2,6), 128.41 (C-2′,6′), 129.51 (C-3′,5′), 128.52 (C-3,4,5), 132.71 (C-1′), 135.4 (C-1), 145.2 (C-4′), 192.7 (C=O).
Minor Isomer: ^{1}H NMR: δ = 2.42 (s, 3 H, CH_3), 3.26 (dd, *J* = 2.0 and 3.1 Hz, 1 H, H-γ), 3.43 (dd, *J* = 2.0 and 3.1 Hz, 1 H, H-β), 3.94 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.33 (d, *J* = 2.0 Hz, 1 H, H-α), 7.25−7.35 (m, 7 H, H-2,3,3′,4,5,5′,6), 7.95 (d, *J* = 8.3 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 21.7 (*C*H_3), 53.9 (C-α), 56.1 (C-δ), 56.4 (C-β), 58.8 (C-γ), 125.58 (C-2,6), 128.45 (C-2′,6′), 128.49 (C-3′,5′), 128.54 (C-4), 128.61 (C-3,5), 132.73 (C-1′), 135.7 (C-1), 145.2 (C-4′), 192.5 (C=O).

Diastereomeric Mixture (36:64) of 4′-Methoxy-α,β:γ,δ-diepoxycinnamylidene-acetophenone (3c)
Major Isomer: ^{1}H NMR: δ = 3.18 (dd, *J* = 1.9 and 4.5 Hz, 1 H, H-γ), 3.34 (dd, *J* = 1.9 and 4.5 Hz, 1 H, H-β), 3.87 (s, 3 H, OCH_3), 3.91 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.29 (d, *J* = 1.9 Hz, 1 H, H-α), 6.97 (d, *J* = 8.9 Hz, 2 H, H-3′,5′), 7.25−7.29 (m, 2 H, H-2,6), 7.32−7.36 (m, 3 H, H-3,4,5), 8.04 (d, *J* = 8.9 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.3 (C-α), 55.4 (O*C*H$_3$), 57.0 (C-δ), 57.4 (C-β), 59.7 (C-γ), 114.02 (C-3′,5′), 125.53 (C-2,6), 128.2 (C-1′), 128.50 (C-3,4,5), 130.7 (C-2′,6′), 135.4 (C-1), 164.2 (C-4′), 191.2 (C=O).
Minor Isomer: ^{1}H NMR: δ = 3.26 (dd, *J* = 2.0 and 3.1 Hz, 1 H, H-γ), 3.43 (dd, *J* = 2.0 and 3.1 Hz, 1 H, H-β), 3.87 (s, 3 H, OCH_3), 3.94 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.31 (d, *J* = 2.0 Hz, 1 H, H-α), 6.97 (d, *J* = 8.8 Hz, 2 H, H-3′,5′), 7.25−7.29 (m, 2 H, H-2,6), 7.32−7.36 (m, 3 H, H-3,4,5), 8.04 (d, *J* = 8.8 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 53.8 (C-α), 55.4 (O*C*H$_3$), 56.1 (C-δ), 56.2 (C-β), 58.8 (C-γ), 113.99 (C-3′,5′), 125.56 (C-2,6), 128.3 (C-1′), 128.52 (C-4), 128.58 (C-3,5), 130.8 (C-2′,6′), 135.7 (C-1), 164.2 (C-4′), 191.4 (C=O).

Diastereomeric Mixture (35:65) of 4′-Fluoro-α,β:γ,δ-diepoxycinnamylideneacetophenone (3d)
Major Isomer: ^{1}H NMR: δ = 3.18 (dd, *J* = 1.9 and 4.6 Hz, 1 H, H-γ), 3.35 (dd, *J* = 1.9 and 4.6 Hz, 1 H, H-β), 3.92 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.28 (d, *J* = 1.9 Hz, 1 H, H-α), 7.19 (dd, J_{H-F} = 8.5 Hz and J_{H-H} = 8.8 Hz, 2 H, H-3′,5′), 7.27−7.30 (m, 2 H, H-2,6), 7.34−7.39 (m, 3 H, H-3,4,5), 8.09 (dd, *J* = 2.2 and 8.8 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.7 (C-α), 57.2 (C-δ), 57.6 (C-β), 59.7 (C-γ), 116.2 (d, J_{C-F} = 24.8 Hz, C-3′,5′), 125.6 (C-2,6), 128.6 (C-3,4,5), 131.2 (d, J_{C-F} = 9.4 Hz, C-2′,6′), 131.6 (d, J_{C-F} = 2.6 Hz, C-1′), 135.7 (C-1), 166.3 (d, J_{C-F} = 291.5 Hz, C-4′), 191.6 (C=O).
Minor Isomer: ^{1}H NMR: δ = 3.28 (dd, *J* = 2.0 and 3.0 Hz, 1 H, H-γ), 3.46 (dd, *J* = 2.0 and 3.0 Hz, 1 H, H-β), 3.95 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.30 (d, *J* = 2.0 Hz, 1 H, H-α), 7.19 (dd, J_{H-F} = 8.5 Hz and J_{H-H} = 8.8 Hz, 2 H, H-3′,5′), 7.27−7.30 (m, 2 H, H-2,6), 7.34−7.39 (m, 3 H, H-3,4,5), 8.11 (dd, *J* = 2.3 and 8.8 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.2 (C-α), 56.3 (C-δ), 56.4 (C-β), 58.7 (C-γ), 116.1 (d, J_{C-F} = 24.8 Hz, C-3′,5′), 125.7 (C-2,6), 128.7 (C-4), 128.8 (C-3,5), 131.3 (d, J_{C-F} = 11.1 Hz, C-2′,6′), 131.7 (d, J_{C-F} = 3.4 Hz, C-1′), 135.4 (C-1), 166.3 (d, J_{C-F} = 291.5 Hz, C-4′), 191.8 (C=O).

Diastereomeric Mixture (33:67) of 4′-Chloro-α,β:γ,δ-diepoxycinnamylideneacetophenone (3e)
Major Isomer: ^{1}H NMR: δ = 3.18 (dd, *J* = 1.9 and 4.6 Hz, 1 H, H-γ), 3.35 (dd, *J* = 1.9 and 4.6 Hz, 1 H, H-β), 3.92 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.27 (d, *J* = 1.9 Hz, 1 H, H-α), 7.26−7.30 (m, 2 H, H-2,6), 7.31−7.38 (m, 3 H, H-3,4,5), 7.49 (d, *J* = 8.7 Hz, 2 H, H-3′,5′), 7.99 (d, *J* = 8.7 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.7 (C-α), 57.2 (C-δ), 57.6 (C-β), 59.6 (C-γ), 125.59 (C-2,6), 128.61 (C-3,4,5), 129.2 (C-3′,5′), 129.84 (C-2′,6′), 133.40 (C-1′), 135.3 (C-1), 140.8 (C-4′), 192.1 (C=O).
Minor Isomer: ^{1}H NMR: δ = 3.28 (dd, *J* = 2.0 and 2.9 Hz, 1 H, H-γ), 3.46 (dd, *J* = 2.0 and 2.9 Hz, 1 H, H-β), 3.95 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.30 (d, *J* = 2.0 Hz, 1 H, H-α), 7.26−7.30 (m, 2 H, H-2,6), 7.31−7.38 (m, 3 H, H-3,4,5), 7.49 (d, *J* = 8.7 Hz, 2 H, H-3′,5′), 8.00 (d, *J* = 8.7 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.2 (C-α), 56.3 (C-δ), 56.4 (C-β), 58.6 (C-γ), 125.62 (C-2,6), 128.74 (C-3,5), 128.68 (C-4), 129.2 (C-3′,5′), 129.81 (C-2′,6′), 133.43 (C-1′), 135.3 (C-1), 140.8 (C-4′), 192.3 (C=O).

Diastereomeric Mixture (32:68) of 4′-Bromo-α,β:γ,δ-diepoxycinnamylideneacetophenone (3f)
Major Isomer: ^{1}H NMR: δ = 3.18 (dd, *J* = 1.8 and 4.6 Hz, 1 H, H-γ), 3.35 (dd, *J* = 1.8 and 4.6 Hz, 1 H, H-β), 3.92 (d, *J* = 1.8 Hz, 1 H, H-δ), 4.27 (d, *J* = 1.8 Hz, 1 H, H-α), 7.26−7.40 (m, 5 H, H-2,3,4,5,6), 7.66 (d, *J* = 8.5 Hz, 2 H, H-3′,5′), 7.92 (d, *J* = 8.5 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.7 (C-α), 57.2 (C-δ), 57.7 (C-β), 59.6 (C-γ), 125.6 (C-2,6), 128.66 (C-3,4,5), 129.6 (C-4′), 129.89 (C-2′,6′), 132.3 (C-3′,5′), 133.84 (C-1′), 135.3 (C-1), 192.4 (C=O).
Minor Isomer: ^{1}H NMR: δ = 3.28 (dd, *J* = 1.8 and 2.5 Hz, 1 H, H-γ), 3.46 (dd, *J* = 1.8 and 2.5 Hz, 1 H, H-β), 3.95 (d, *J* = 1.8 Hz, 1 H, H-δ), 4.29 (d, *J* = 1.8 Hz, 1 H, H-α), 7.26−7.40 (m, 5 H, H-2, -3, -4, -5, -6), 7.66 (d, *J* = 8.5 Hz, 2 H, H-3′,5′), 7.92 (d, *J* = 8.5 Hz, 2 H, H-2′,6′). − ^{13}C NMR: δ = 54.2 (C-α), 56.3 (C-δ), 56.4 (C-β), 58.6 (C-γ), 125.7 (C-2,6), 128.70 (C-4), 128.79 (C-3,5), 129.6 (C-4′), 129.94 (C-2′,6′), 132.3 (C-3′,5′), 133.87 (C-1′), 135.6 (C-1), 192.5 (C=O).

Reactions of (*E,E*)-Cinnamylideneacetophenones 1c,d with One Equivalent of Dimethyldioxirane According to the Procedure Described for the Diepoxides 3a−f: The obtained mixtures were analysed by NMR spectroscopy and revealed the presence of the α,β-monoepoxides **2c,d** and diastereomeric mixtures of the α,β:γ,δ-diepoxides **3c,d** in approximately 2:1 ratio. Here we present the main characteristics of the monoepoxides **2c,d**.

4′-Methoxy-α,β-epoxycinnamylideneacetophenone (2c): ^{1}H NMR: δ = 3.73 (dd, *J* = 1.9 and 7.9 Hz, 1 H, H-β), 4.27 (d, *J* = 1.9 Hz, 1 H, H-α), 6.03 (dd, *J* = 7.9 and 16.0 Hz, 1 H, H-γ), 6.88 (d, *J* = 16.0 Hz, 1 H, H-δ). − ^{13}C NMR: δ = 59.0 (C-α), 59.6 (C-β), 124.6 (C-γ), 135. 8 (C-1), 136.2 (C-δ), 191.4 (C=O).

4′-Fluoro-α,β-epoxycinnamylideneacetophenone (2d): ^{1}H NMR: δ = 3.74 (dd, *J* = 1.8 and 7.9 Hz, 1 H, H-β), 4.26 (d, *J* = 1.8 Hz, 1 H, H-α), 6.03 (dd, *J* = 7.9 and 15.9 Hz, 1 H, H-γ), 6.90 (d, *J* = 15.9 Hz, 1 H, H-δ). − ^{13}C NMR: δ = 59.3 (C-α), 59.8 (C-β), 124.2 (C-γ), 135. 7 (C-1), 136.7 (C-δ), 191.8 (C=O).

Reactions of (*E,E*)-2′-Hydroxycinnamylideneacetophenones 4a−d With Dimethyldioxirane According to the Procedure Described for the Preparation of the Diepoxides 3a−f: The NMR analysis of the reaction mixtures revealed the presence of the γ,δ-monoepoxides **5a−d** and the α,β,γ,δ-diepoxides **6a−d**. Here we only consider the assignments unequivocally made for these diepoxides **6a−d**. These mixtures were analysed by preparative silica gel thin layer chromatography (eluent: 1:1 mixture of light petroleum ether/dichloromethane), leading to the isolation of the γ,δ-monoepoxides **5a−d** and the coumaranone derivatives **7a−d**.

2′-Hydroxy-γ,δ-epoxycinnamylideneacetophenone (5a): ^{1}H NMR: δ = 3.63 (ddd, *J* = 0.5, 1.6 and 6.2 Hz, 1 H, H-γ), 3.90 (d, *J* =

1.6 Hz, 1 H, H-δ), 7.09 (dd, *J* = 6.2 and 15.1 Hz, 1 H, H-β), 6.93 (ddd, *J* = 1.1, 7.2 and 8.1 Hz, 1 H, H-5′), 7.02 (dd, *J* = 1.1 and 8.5 Hz, 1 H, H-3′), 7.31−7.42 (m, 5 H, H-2,3,4,5,6), 7.40 (d, *J* = 15.1 Hz, 1 H, H-α), 7.51 (ddd, *J* = 1.6, 7.2 and 8.5 Hz, 1 H, H-4′), 7.82 (dd, *J* = 1.6 and 8.1 Hz, 1 H, H-6′), 12.55 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 61.1 (C-γ), 61.8 (C-δ), 118.6 (C-3′), 119.0 (C-5′), 119.4 (C-1′), 125.3 (C-α), 125.5 (C-2,6), 128.7 (C-3,5), 128.8 (C-4), 129.9 (C-6′), 135.9 (C-1), 136.8 (C-4′), 144.2 (C-β), 163.6 (C-2′), 193.0 (C=O).

2′-Hydroxy-4′-methyl-γ,δ-epoxycinnamylideneacetophenone (5b): ^{1}H NMR: δ = 2.37 (s, 3 H, C*H*$_3$), 3.62 (dd, *J* = 1.7 and 6.0 Hz, 1 H, H-γ), 3.90 (d, *J* = 1.7 Hz, 1 H, H-δ), 6.83 (br. s, 1 H, H-3′), 6.74 (dd, *J* = 1.4 and 8.2 Hz, 1 H, H-5′), 7.06 (dd, *J* = 6.0 and 15.3 Hz, 1 H, H-β), 7.30−7.42 (m, 5 H, H-2,3,4,5,6), 7.37 (d, *J* = 15.3 Hz, 1 H, H-α), 7.70 (d, *J* = 8.2 Hz, 1 H, H-6′), 12.62 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 22.0 (*C*H$_3$), 61.1 (C-γ), 61.8 (C-δ), 115.9 (C-1′), 118.6 (C-3′), 120.4 (C-5′), 124.1 (C-α), 124.2 (C-2,6), 127.3 (C-3,5), 127.4 (C-4), 129.8 (C-6′), 134.6 (C-1), 147.7 (C-β), 148.6 (C-4′), 163.8 (C-2′), 192.3 (C=O).

5′-Fluoro-2′-hydroxy-γ,δ-epoxycinnamylideneacetophenone (5c): ^{1}H NMR: δ = 3.64 (dd, *J* = 0.60, 1.8 and 6.0 Hz, 1 H, H-γ), 3.90 (d, *J* = 1.8 Hz, 1 H, H-δ), 6.99 (dd, $J_{H\text{-}F}$ = 4.6 Hz and $J_{H\text{-}H}$ = 9.2 Hz, 1 H, H-3′), 7.12 (dd, *J* = 6.0 and 15.1 Hz, 1 H, H-β), 7.26 (ddd, $J_{H\text{-}F}$ = 8.9 Hz and $J_{H\text{-}H}$ = 3.1 and 9.2 Hz, 1 H, H-3′), 7.31−7.42 (m, 5 H, H-2,3,4,5,6), 7.35 (d, *J* = 15.1 Hz, 1 H, H-α), 7.48 (dd, $J_{H\text{-}F}$ = 8.9 Hz and $J_{H\text{-}H}$ = 3.1 Hz, 1 H, H-6′), 12.29 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 60.9 (C-γ), 61.9 (C-δ), 114.7 (d, $J_{C\text{-}F}$ = 23.5 Hz, C-6′), 118.8 (d, $J_{C\text{-}F}$ = 6.2 Hz, C-1′), 119.9 (d, $J_{C\text{-}F}$ = 7.2 Hz, C-3′), 124.4 (d, $J_{C\text{-}F}$ = 23.7 Hz, C-4′), 124.8 (C-α), 125.5 (C-2,6), 128.7 (C-3,5), 128.8 (C-4), 135.9 (C-1), 145.2 (C-β), 154.8 (d, $J_{C\text{-}F}$ = 238.7 Hz, C-5′), 159.8 (d, $J_{C\text{-}F}$ = 1.1 Hz, C-2′), 192.2 (d, $J_{C\text{-}F}$ = 2.9 Hz, C=O).

5′-Chloro-2′-hydroxy-γ,δ-epoxycinnamylideneacetophenone (5d): ^{1}H NMR: δ = 3.65 (dd, *J* = 1.5 and 5.9 Hz, 1 H, H-γ), 3.91 (d, *J* = 1.5 Hz, 1 H, H-δ), 6.98 (d, *J* = 8.9 Hz, 1 H, H-3′), 7.13 (dd, *J* = 5.9 and 15.0 Hz, 1 H, H-β), 7.31−7.42 (m, 5 H, H-2,3,4,5,6), 7.32 (d, *J* = 15.0 Hz, 1 H, H-α), 7.45 (dd, *J* = 2.6 and 8.9 Hz, 1 H, H-4′), 7.78 (d, *J* = 2.6 Hz, 1 H, H-6′), 12.46 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 60.9 (C-γ), 62.0 (C-δ), 120.0 (C-1′), 120.2 (C-3′), 123.7 (C-5′), 124.6 (C-α), 125.6 (C-2,6), 128.7 (C-3,5), 128.8 (C-4), 129.1 (C-6′), 135.8 (C-1), 136.6 (C-4′), 145.4 (C-β), 162.1 (C-2′), 192.1 (C=O).

Diastereomeric Mixture (88:12) of 2′-Hydroxy-α,β:γ,δ-diepoxycinnamylideneacetophenone (6a)

Major Isomer: ^{1}H NMR: δ = 3.21 (dd, *J* = 1.8 and 4.8 Hz, 1 H, H-γ), 3.43 (dd, *J* = 1.7 and 4.8 Hz, 1 H, H-β), 3.94 (d, *J* = 1.8 Hz, 1 H, H-δ), 4.40 (d, *J* = 1.7 Hz, 1 H, H-α), 6.77 (dd, *J* = 1.2 and 7.94 (d, *J* = 1.3 and 8.1 Hz, 1 H, H-6′), 11.77 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 53.5 (C-α), 57.3 (C-δ), 58.2 (C-β), 59.5 (C-γ), 162.6 (C-2′), 197.3 (C=O).

Minor Isomer: ^{1}H NMR: δ = 3.31 (dd, *J* = 2.0 and 2.7 Hz, 1 H, H-γ), 3.53 (dd, *J* = 2.1 and 2.7 Hz, 1 H, H-β), 3.98 (d, *J* = 2.0 Hz, 1 H, H-δ), 4.42 (d, *J* = 2.1 Hz, 1 H, H-α), 11.85 (s, 1 H, 2′-OH).

Diastereomeric Mixture (86:14) of 2′-Hydroxy-4′-methyl-α,β:γ,δ-diepoxycinnamylideneacetophenone (6b)

Major Isomer: ^{1}H NMR: δ = 2.33 (s, 3 H, C*H*$_3$), 3.19 (dd, *J* = 1.9 and 4.3 Hz, 1 H, H-γ), 3.39 (dd, *J* = 1.9 and 4.3 Hz, 1 H, H-β), 3.91 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.34 (d, *J* = 1.9 Hz, 1 H, H-α), 6.77 (dd, *J* = 1.2 and 8.2 Hz, 1 H, H-5′), 6.82 (br. s, 1 H, H-3′), 7.79 (d, *J* = 8.2 Hz, 1 H, H-6′), 11.80 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 22.0 (*C*H$_3$), 53.3 (C-α), 57.1 (C-δ), 57.9 (C-β), 59.4 (C-γ), 118.6 (C-3′), 120.8 (C-5′), 125.6 (C-2,6), 129.2 (C-6′), 135.3 (C-1), 149.5 (C-4′), 162.6 (C-2′), 196.6 (C=O).

Minor Isomer: ^{1}H NMR: δ = 2.34 (s, 3 H, C*H*$_3$), 3.28 (dd, *J* = 1.9 and 2.8 Hz, 1 H, H-γ), 3.49 (dd, *J* = 1.9 and 2.8 Hz, 1 H, H-β), 3.94 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.35 (d, *J* = 1.9 Hz, 1 H, H-α), 11.83 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 21.9 (*C*H$_3$), 52.9 (C-α), 56.2 (C-δ), 56.6 (C-β), 58.5 (C-γ), 125.4 (C-2,6), 135.9 (C-1), 149.6 (C-4′), 163.2 (C-2′), 196.7 (C=O).

Diastereomeric Mixture (60:40) of 5′-Fluoro-2′-hydroxy-α,β:γ,δ-diepoxycinnamylidene-acetophenone (6c)

Major Isomer: ^{1}H NMR: δ = 3.20 (dd, *J* = 1.8 and 4.4 Hz, 1 H, H-γ), 3.41 (dd, *J* = 1.8 and 4.4 Hz, 1 H, H-β), 3.93 (d, *J* = 1.7 Hz, 1 H, H-δ), 4.29 (d, *J* = 1.7 Hz, 1 H, H-α), 11.52 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 53.8 (C-α), 57.3 (C-δ), 58.29 (C-β), 59.4 (C-γ), 158.9 (C-2′), 196.9 (d, $J_{C\text{-}F}$ = 2.9 Hz, C=O).

Minor Isomer: ^{1}H NMR: δ = 3.31 (dd, *J* = 1.9 and 2.2 Hz, 1 H, H-γ), 3.52 (dd, *J* = 2.0 and 2.2 Hz, 1 H, H-β), 3.96 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.31 (d, *J* = 2.0 Hz, 1 H, H-α), 11.55 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 53.4 (C-α), 56.5 (C-δ), 56.9 (C-β), 59.33 (C-γ), 158.9 (C-2′), 197.1 (d, $J_{C\text{-}F}$ = 2.9 Hz, C=O).

Diastereomeric Mixture (63:37) of 5′-Chloro-2′-hydroxy-α,β:γ,δ-diepoxycinnamylidene-acetophenone (6d)

Major Isomer: ^{1}H NMR: δ = 3.20 (dd, *J* = 1.7 and 4.4 Hz, 1 H, H-γ), 3.42 (dd, *J* = 1.7 and 4.4 Hz, 1 H, H-β), 3.94 (d, *J* = 1.7 Hz, 1 H, H-δ), 4.31 (d, *J* = 1.9 Hz, 1 H, H-α), 6.99 (d, *J* = 8.9 Hz, 1 H, H-3′), 7.27−7.39 (m, 5 H, H-2,3,4,5,6), 7.48 (dd, *J* = 2.4 and 8.9 Hz, 1 H, H-4′), 7.90 (d, *J* = 2.4 Hz, 1 H, H-6′), 11.68 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 53.6 (C-α), 57.2 (C-δ), 58.3 (C-β), 59.3 (C-γ), 119.06 (C-1′), 120.35 (C-3′), 124.2 (C-5′), 125.6 (C-2,6), 135.1 (C-1), 137.38 (C-4′), 161.0 (C-2′), 196.8 (C=O).

Minor Isomer: ^{1}H NMR: δ = 3.31 (dd, *J* = 1.9 and 2.2 Hz, 1 H, H-γ), 3.53 (dd, *J* = 2.0 and 2.2 Hz, 1 H, H-β), 3.96 (d, *J* = 1.9 Hz, 1 H, H-δ), 4.33 (d, *J* = 2.0 Hz, 1 H, H-α), 6.96 (d, *J* = 8.7 Hz, 1 H, H-3′), 7.27−7.39 (m, 5 H, H-2,3,4,5,6), 7.43 (dd, *J* = 2.4 and 8.7 Hz, 1 H, H-4′), 7.91 (d, *J* = 2.4 Hz, 1 H, H-6′), 11.71 (s, 1 H, 2′-OH). − ^{13}C NMR: δ = 53.2 (C-α), 56.4 (C-δ), 56.9 (C-β), 58.3 (C-γ), 119.09 (C-1′), 120.32 (C-3′), 124.2 (C-5′), 125.5 (C-2,6), 135.4 (C-1), 137.38 (C-4′), 161.0 (C-2′), 197.0 (C=O).

Diastereomeric Mixture (58:42) of 2-(γ-Phenyl-α-hydroxy-β,γ-epoxypropyl)coumaranone (7a)

Major Isomer: ^{1}H NMR: δ = 3.38 (dd, *J* = 2.1 and 4.4 Hz, 1 H, H-2′), 4.08 (d, *J* = 2.1 Hz, 1 H, H-3′), 4.42−4.44 (m, 1 H, H-1′), 4.74 (d, *J* = 2.4 Hz, 1 H, H-2), 7.06−7.21 (m, H-5 and H-7), 7.30−7.41 (m, H-2′′, -3′′, -4′′, -5′′, -6′′), 7.59−7.70 (m, H-4 and H-6). − ^{13}C NMR: δ = 56.4 (C-3′), 61.4 (C-2′), 69.6 (C-1′), 84.41 (C-2), 113.4 (C-7), 121.4 (C-9), 122.3 (C-5), 124.27 (C-4), 125.7 (C-2′′, -6′′), 128.0−129.1 (C-3′′, -4′′, -5′′), 136.2 (C-1′′), 138.29 (C-6), 173.5 (C-8), 199.5 (C=O).

Minor Isomer: ^{1}H NMR: δ = 3.25 (dd, *J* = 2.1 and 3.5 Hz, 1 H, H-2′), 4.10 (d, *J* = 2.1 Hz, 1 H, H-3′), 4.42−4.44 (m, 1 H, H-1′), 4.78 (d, *J* = 4.2 Hz, 1 H, H-2), 7.06−7.21 (m, H-5 and H-7), 7.30−7.41 (m, H-2′′, -3′′, -4′′, -5′′, -6′′), 7.59−7.70 (m, H-4 and H-6). − ^{13}C NMR: δ = 55.5 (C-3′), 60.3 (C-2′), 69.8 (C-1′), 84.37 (C-2), 113.5 (C-7), 122.6 (C-5), 122.4 (C-9), 124.31 (C-4), 125.6 (C-2′′, -6′′), 128.0−129.1 (C-3′′, -4′′, -5′′), 136.6 (C-1′′), 138.33 (C-6), 173.5 (C-8), 199.5 (C=O).

Diastereomeric Mixture (55:45) of 6-Methyl-2-(γ-phenyl-α-hydroxy-β,γ-epoxypropyl)coumaranone (7b)

Major Isomer: ^{1}H NMR: δ = 2.45 (s, 3 H, C*H*$_3$), 3.36 (dd, *J* = 2.1 and 4.4 Hz, 1 H, H-2′), 4.07 (d, *J* = 2.1 Hz, 1 H, H-3′), 4.42 (dd, *J* = 2.4 and 4.4 Hz, 1 H, H-1′), 4.73 (d, *J* = 2.4 Hz, 1 H, H-2),

6.95 (br. d, J = 7.9 Hz, H-5), 6.99 (br. s, 1 H, H-7), 7.27−7.42 (m, 5 H, H-2′′, -3′′, -4′′, -5′′, -6′′), 7.56 (d, J = 7.9 Hz, 1 H, H-4). − ^{13}C NMR: δ = 22.6 (CH_3), 56.3 (C-3′), 61.5 (C-2′), 69.5 (C-1′), 84.6 (C-2), 113.4 (C-7), 119.0 (C-9), 124.0 and 123.9 (C-4 and C-5), 125.7 (C-2′′, -6′′), 128.36, 128.43 and 128.5 (C-3′′, -4′′, -5′′), 136.3 (C-1′′), 150.5 (C-6), 174.0 (C-8), 198.8 (C=O).

Minor Isomer: ^{1}H NMR: δ = 2.42 (s, 3 H, CH_3), 3.24 (dd, J = 2.1 and 3.7 Hz, 1 H, H-2′), 4.10 (d, J = 2.1 Hz, 1 H, H-3′), 4.39 (dd, J = 3.7 and 4.3 Hz, 1 H, H-1′), 4.76 (d, J = 4.3 Hz, 1 H, H-2), 6.90 (br. d, J = 7.7 Hz, H-5), 6.99 (br. s, 1 H, H-7), 7.27−7.42 (m, 5 H, H-2′′, -3′′, -4′′, -5′′, -6′′), 7.53 (d, J = 7.7 Hz, 1 H, H-4). − ^{13}C NMR: δ = 22.6 (CH_3), 55.4 (C-3′), 60.4 (C-2′), 69.8 (C-1′), 84.5 (C-2), 113.5 (C-7), 118.3 (C-9), 123.9 and 123.8 (C-4 and C-5), 125.7 (C-2′′, -6′′), 128.36, 128.43 and 128.5 (C-3′′, -4′′, -5′′), 136.2 (C-1′′), 150.6 (C-6), 173.5 (C-8), 198.5 (C=O).

Diastereomeric Mixture (71:29) of 5-Fluoro-2-(γ-phenyl-α-hydroxy-β,γ-epoxypropyl)coumaranone (7c)

Major Isomer: ^{1}H NMR: δ = 3.37 (dd, J = 2.1 and 4.3 Hz, 1 H, H-2′), 3.99 (d, J = 2.1 Hz, 1 H, H-3′), 4.42−4.45 (m, 1 H, H-1′), 4.79 (d, J = 2.3 Hz, 1 H, H-2), 7.16−7.47 (m, 8 H, H-2′′, -3′′, -4′′, -4, -5′′, -6′′, -6, -7).

Minor Isomer: ^{1}H NMR: δ = 3.24 (dd, J = 2.0 and 3.9 Hz, 1 H, H-2′), 3.96 (d, J = 2.0 Hz, 1 H, H-3′), 4.42−4.45 (m, 1 H, H-1′), 4.78 (d, J = 3.1 Hz, 1 H, H-2), 7.16−7.47 (m, 8 H, H-2′′, -3′′, -4′′, -4, -5′′, -6′′, -6, -7).

Diastereomeric Mixture (51:49) of 5-Chloro-2-(γ-phenyl-α-hydroxy-β,γ-epoxypropyl)coumaranone (7d)

Major Isomer: ^{1}H NMR: δ = 3.36 (dd, J = 2.1 and 4.5 Hz, 1 H, H-2′), 4.04 (d, J = 2.1 Hz, 1 H, H-3′), 4.39−4.42 (m, 1 H, H-1′), 4.74 (d, J = 2.1 Hz, 1 H, H-2), 7.11 (d, J = 7.6 Hz, 1 H, H-7), 7.27−7.33 (m, 5 H, H-2′′, -3′′, -4′′, -5′′, -6′′), 7.53 (dd, J = 2.3 and 7.6 Hz, 1 H, H-6), 7.62 (d, J = 2.3 Hz, 1 H, H-7). − ^{13}C NMR: δ = 56.0 (C-3′), 61.3 (C-2′), 69.6 (C-1′), 85.5 (C-2), 114.7 (C-7), 122.43 (C-9), 123.6 (C-4), 125.57, 125.69 and 125.71 (C-2′′, -6′′), 128.36−129.96 (C-3′′, -4′′, -5′′), 136.1 (C-1′′), 138.0 (C-6), 171.8 (C-8), 198.5 (C=O).

Minor Isomer: ^{1}H NMR: δ = 3.24 (dd, J = 2.2 and 3.5 Hz, 1 H, H-2′), 4.05 (d, J = 2.2 Hz, 1 H, H-3′), 4.39−4.42 (m, 1 H, H-1′), 4.82 (d, J = 2.3 Hz, 1 H, H-4), 7.14 (d, J = 8.0 Hz, 1 H, H-7), 7.27−7.33 (m, 5 H, H-2′′, -3′′, -4′′, -5′′, -6′′), 7.59 (dd, J = 2.4 and 8.0 Hz, 1 H, H-6), 7.60 (d, J = 2.4 Hz, 1 H, H-7). − ^{13}C NMR: δ = 55.8 (C-3′), 60.0 (C-2′), 69.9 (C-1′), 85.6 (C-2), 114.7 (C-7), 122.40 (C-9), 123.7 (C-4), 125.57, 125.69 and 125.71 (C-2′′, -6′′), 128.36−129.96 (C-3′′, -4′′, -5′′), 136.0 (C-1′′), 138.0 (C-6), 171.3 (C-8), 197.7 (C=O).

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