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p*H*-SENSITIVE EXCITON CHIRALITY CHROMOPHORE. SOLVATOCHROMIC EFFECTS ON CIRCULAR DICHROISM SPECTRA

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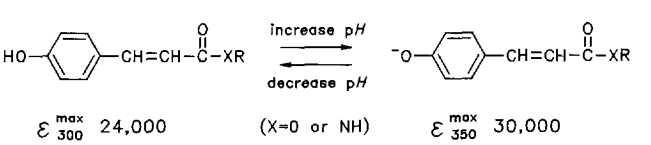
Abstract: Diesters (**1** and **3**) of (1*S*,2*S*) and (1*R*,2*R*)-cyclohexanediol and diamides (**2** and **4**) of (1*S*,2*S*) and (1*R*,2*R*)-diaminocyclohexane with *p*-hydroxycinnamic acid exhibit intense bisignate circular dichroism spectra in CH_3OH: **1** $\Delta\varepsilon$ +55 (323 nm), −34 (287 nm); **2** $\Delta\varepsilon$ +75 (318 nm), −55 (281 nm) and in $(CH_3)_2SO$: **1** $\Delta\varepsilon$ +53 (328 nm), −33 (292 nm); **2** $\Delta\varepsilon$ +65 (319 nm), −50 (280 nm). Added NaOH causes a bathochromic shift of ~50 nm in CH_3OH and ~80-90 nm in $(CH_3)_2SO$. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

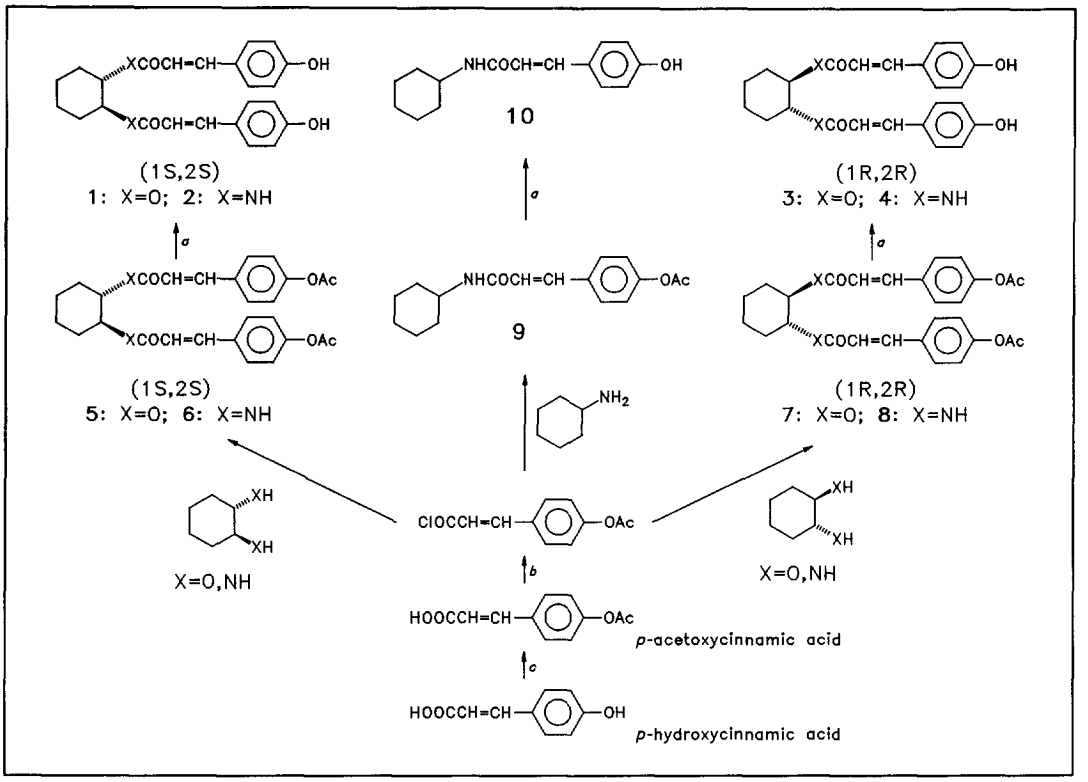
The search for new types of chromophores useful in forming derivatives of diols and diamines for exciton chirality[1] studies has uncovered a variety of carboxylic acids ranging from *para*-substituted benzoic and cinnamic acids to naphthoic and anthroic acids,[2] from dipyrrinone acids[3] to porphyrin acids.[4,5] The last are especially useful for long-range exciton coupling. In the current work, we focussed attention on the *p*-hydroxycinnamate chromophore for exploring a potential p*H* shift on exciton Cotton effects. Previously, *p*-methoxy and *p*-dimethyl-amino cinnamic acid esters have been used in exciton studies,[2] but to the best of our knowledge, the *p*-hydroxy has not. Yet, one can anticipate that its carboxylic acid esters and amides should exhibit large bathochromic ultraviolet (UV) and circular dichroism (CD) spectral shifts in the neutral to basic p*H* range. Consequently, we prepared *p*-acetoxycinnamic acid as the key chromophore to be used in our syntheses.



RESULTS AND DISCUSSION

Synthesis. As outlined in the Synthetic Scheme, *p*-hydroxycinnamic acid was acetylated in 89% yield using acetic anhydride in pyridine.[6] The product was converted with thionyl chloride to the corresponding acid chloride, which was reacted smoothly with (1*S*,2*S*) or (1*R*,2*R*)-*trans*-cyclohexanediol in dry dichloromethane

SYNTHETIC SCHEME



[a] CH_3ONa, then HCl; [b] $SOCl_2$; [c] $(CH_3CO)_2O$, Pyridine.

in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine to afford bis-*p*-acetoxycinnamate esters **5** or **7** in 83-91% isolated yield. Using the same procedure, bis-amides **6** or **8** were prepared from (1*S*,2*S*) or (1*R*,2*R*)-*trans*-1,2-diaminocyclohexane in 83-89% isolated yield. Amide formation using unprotected *p*-hydroxycinnamic acid has been recently reported.[7] The *p*-acetyl group could be cleaved selectively in each derivative using 1.5 equivalents sodium methoxide in chloroform-methanol.[8] The resulting diesters **1** and **3** were purified by radial chromatography (65-77% yield); the diamides **2** and **4** were purified by crystallization from ether-methanol (84-88% yield). For purposes of spectral comparison the mono-amides (**9** and **10**) of cyclohexylamine were prepared similarly.

CD Spectra. The CD spectra of the bis-*p*-acetoxycinnamate ester (**5**) of (1*S*,2*S*)-cyclohexanediol (Fig. 1, spectrum 1) and the bis-*p*-hydroxycinnamate ester (**1**) (Fig. 1, spectra 2-5) show the typical bisignate behavior of an exciton system.[1] In this case, a positive exciton chirality is observed throughout Fig. 1, as predicted for the (1*S*,2*S*) configuration from the exciton chirality rule.[1] In addition, there are strong spectral shifts. The *p*-acetoxy derivative (**5**) in methanol is blue-shifted by ~30 nm from the *p*-hydroxy derivative (**1**). A similar shift was also observed in chloroform solvent (Table 1). However, there is little difference between spectra of **5** run in chloroform and methanol, and there is little difference between spectra of **1** run in chloroform and

methanol. An entirely analogous CD behavior is found in the bis-amides **6** and **2** (Fig. 2 and Table 1). This type of spectral shift *p*-OH and *p*-OAc has been noted previously on the intramolecular charge transfer UV absorption band of benzoic acids and cinnamic acids.

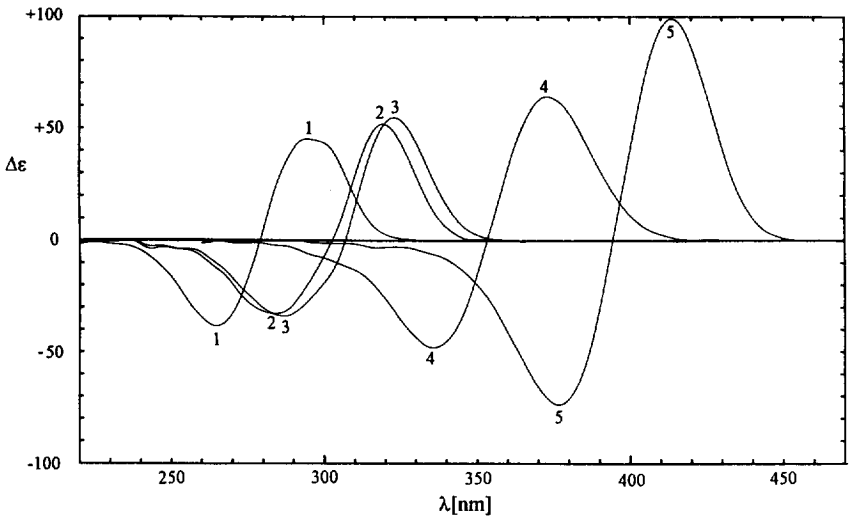


FIGURE 1. Circular dichroism spectra of 2.4 × 10^{-5} M solutions of (1*S*,2*S*)-**5** in methanol (spectrum 1) and (1*S*,2*S*)-**1** in chloroform (spectrum 2), methanol (spectrum 3), 0.1 M sodium hydroxide in methanol (spectrum 4), and dimethyl sulfoxide containing 0.1 M sodium hydroxide in methanol 50:1 v/v (spectrum 5) at 22°C.

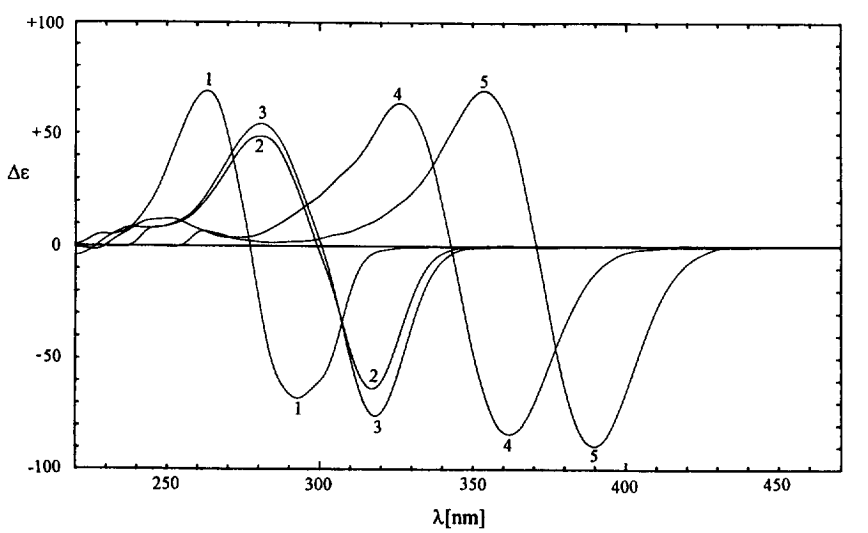


FIGURE 2. Circular dichroism spectra of 3.4 × 10^{-5} M solutions of (1*R*,2*R*)-**8** in methanol (spectrum 1) and (1*R*,2*R*)-**4** in chloroform (spectrum 2), methanol (spectrum 3), 0.1 M sodium hydroxide in methanol (spectrum 4), and dimethyl sulfoxide containing 0.1 M sodium hydroxide in methanol 50:1 v/v (spectrum 5) at 22°C.

TABLE 1. Solvent Dependence of Circular Dichroism and UV Spectral Data from 1.5×10^{-5} M Solutions of Diesters **1** and **3** and Diamides **2** and **4** at 22°C.

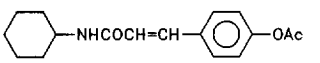
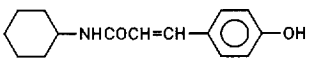
Diester or Diamide	Solvent	CD			UV			
		$\Delta\epsilon^{max}$ (λ_1)	λ_2 at $\Delta\epsilon=0$	$\Delta\epsilon^{max}$ (λ_3)	ϵ^{max}	λ (nm)	ϵ^{max}	λ (nm)
1	$CHCl_3$	+51.7 (319)	303	−32.9 (284)	41000	310	39900	301
3		−51.8 (320)	303	+32.4 (284)	41000	310	39700	301^{sh}
2		+64.5 (317)	300	−50.6 (280)	40100	308^{sh}	44300	292
4		−63.6 (317)	299	+48.7 (281)	38600	308^{sh}	43400	292
1	CH_3OH	+54.5 (323)	307	−34.0 (287)	44900	311	40500	301^{sh}
3		−55.1 (323)	307	+33.4 (287)	45000	311	40900	300^{sh}
2		+75.0 (318)	301	−55.0 (281)	44400	307	46600	292
4		−75.7 (318)	301	+54.3 (281)	43900	308	45900	293
1	$(CH_3)_2SO$	+52.7 (328)	312	−33.1 (292)	44700	315	38000	302^{sh}
2		+64.6 (319)	301	−50.4 (280)	42000	309^{sh}	49000	293
1	0.1 M NaOH in CH_3OH	+63.9 (373)	353	−48.2 (336)	56500	359	16700	311
3		−64.2 (374)	353	+48.0 (336)	56600	360	16700	311
2		+83.6 (362)	343	−64.8 (327)	57700	345	27700	312^{sh}
4		−84.1 (362)	343	+63.5 (326)	57300	346	26600	313^{sh}
1	$(CH_3)_2SO$ containing 2% by vol 0.1 M NaOH in CH_3OH	+99.0 (414)	394	−74.0 (377)	70600	403	11500	323
3		−99.1 (412)	393	+73.8 (375)	69200	403	11100	323
2		+90.0 (391)	371	−69.0 (354)	62700	376	22400	326
4		−89.7 (390)	371	+68.9 (353)	63900	375	22700	325
5	$CHCl_3$	+43.6 (296)	280	−36.6 (266)	40500	283	—	—
7		−46.2 (295)	280	+37.0 (267)	40600	283	—	—
6		+59.0 (293)	279	−61.1 (264)	47200	275	—	—
8		−59.7 (294)	279	+58.4 (264)	47600	275	—	—
5	CH_3OH	+45.2 (295)	280	−38.5 (265)	42900	281	—	—
7		−48.8 (295)	280	+40.6 (265)	43000	281	—	—
6		+66.4 (293)	277	−69.4 (262)	50900	273	—	—
8		−67.9 (293)	277	+68.9 (263)	51500	273	—	—

More interesting are the spectral shifts in **1** (Fig. 1, spectra 4 and 5) and **4** (Fig. 2, spectra 4 and 5) that occur when the *p*-OH group is deprotonated. As might be expected, the CD spectra in pure methanol (Figs. 1 and 2, spectra 3) are strongly shifted (by ~50 nm) to longer wavelengths in methanol containing NaOH, *cf* spectra 3 and 4 of Figures 1 and 2. More unusual, however, are the spectral shifts in basified dimethyl sulfoxide (spectra 5), where a nearly 90 nm bathochromic shift is observed relative to CDs of the diester or diamide in pure dimethylsulfoxide (Table 1), which are essentially identical to the CDs in pure methanol. This unusual solvatochromic effect[9,10] on the phenoxide, which may not have been observed previously in exciton systems leads not only to a strong bathochromic spectral shift in dimethylsulfoxide *vs* methanol but also to a considerable enhancement of $\Delta\epsilon^{max}$.

The solvatochromic effect may also be seen on the non-exciton system **10**, which exhibits the expected UV spectral shift (~40 nm) upon deprotonation of the *p*-OH group in methanol and an additional 30 nm shift

when deprotonated in dimethylsulfoxide (Table 2). Yet, again the UV spectra of the protonated forms are very similar in pure methanol and in dimethylsulfoxide.

TABLE 2. UV Spectral Data for Monoamides **9** and **10**.

	 **9**		 **10**			
Solvent	ε^{max}	λ (nm)	ε^{max}	λ (nm)	ε^{max}	λ (nm)
$CHCl_3$	24300	278	19900	307^{sh}	22300	291
CH_3OH	27500	277	22900	307	23600	292
$(CH_3)_2SO$	24600	276	20300	308^{sh}	23300	293
0.1 M NaOH/CH_3OH	—	—	29700	347	14200	313^{sh}
$(CH_3)_2SO$/NaOH[a]	—	—	31900	378	10800	327

[a] $(CH_3)_2SO$ containing 2% (vol) of a solution of 0.1 M NaOH in CH_3OH

CONCLUDING COMMENTS

The *p*-hydroxycinnamate chromophore has been shown to exhibit the expected excellent p*H*-sensitive spectral shifts in its exciton coupling CD and UV spectra of the diesters of (1*R*,2*R*) and (1*S*,2*S*)-*trans*-cyclohexanediol and the diamides of (1*R*,2*R*) and (1*S*,2*S*)-*trans*-diaminocyclohexane. An unusual solvatochromic effect on the phenoxide form in dimethylsulfoxide solvent leads to ~90 nm bathochromic shifts and 20-40% enhancements of $\Delta\varepsilon^{max}$. These findings indicate *p*-hydroxycinnamic acid may be useful for exciton chirality studies where red-shifted chromophores are important.[2]

EXPERIMENTAL

General. All circular dichroism spectra were recorded on a JASCO J-600 instrument, and all UV-vis spectra were recorded on a Cary 219 spectrophotometer. NMR spectra were obtained on a GE GN-300 spectrometer operating at 300 MHz. $CDCl_3$ solvent (unless otherwise noted) was used and chemical shifts were reported in δ ppm referenced to residual $CHCl_3$ ^1H signal at 7.26 ppm and ^{13}C signal at 77.00 ppm. J-modulated spin-echo experiment (*A*ttached *P*roton *T*est) was used to obtain ^{13}C-NMR spectra. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Radial chromatography was carried out on Merck Silica gel PF_{254} with $CaSO_4$ preparative layer grade, using a Chromatotron (Harrison Research, Inc., Palo Alto, CA). Melting points were determined on a Mel-Temp capillary apparatus and are uncorrected. Combustion analyses were carried out by Desert Analytics, Tucson, AZ.

Spectral data were obtained in spectral grade solvents (Aldrich or Fischer). Enantiomerically pure (1*R*,2*R*) and (1*S*,2*S*)-*trans*-1,2-cyclohexanediol and 1,2-diaminocyclohexane were from Fluka; *trans-p*-hydroxycinnamic acid was from Acros.

***p*-Acetoxycinnamic acid.**[6] To a cooled with ice bath solution of 16.42 g (0.1 mol) *p*-hydroxycinnamic acid in 100 mL of dry pyridine was added 28.3 mL (0.3 mol) of acetic anhydride, and the mixture was stirred at room temperature for 12 h. The mixture was poured into 150 mL of ice water and slowly acidified with conc. HCl. The precipitate was filtered, washed with H_2O (4 x 20 mL) and recrystallized from ethanol to afford 18.32 g (89%) of *p*-acetoxycinnamic acid. It had mp 210-212°C. ^{1}H-NMR ($(CD_3)_2SO$): δ 2.26 (s, 3H), 6.50 (d, 1H, J=16.0 Hz), 7.16 (d, 2H, J=8.4 Hz), 7.58 (d, 1H, J=16.0 Hz), 7.73 (d, 2H, J=8.4 Hz), 12.44 (br.s, 1H) ppm; ^{13}C-NMR ($(CD_3)_2SO$): δ 20.92, 119.34, 122.43, 129.50, 131.98, 143.05, 151.88, 167.64, 169.11 ppm.

General procedure for acylation with *p*-acetoxycinnamic acid. *p*-Acetoxycinnamic acid (618 mg, 3 mmol) was refluxed for 3h with 6 mL of thionyl chloride. Excess $SOCl_2$ was removed under water aspirator vacuum and co-evaporated twice with 10 mL portions of dry benzene. Thus obtained acid chloride was dissolved in 5 mL of dry CH_2Cl_2 and added to a cooled with ice bath solution of 1 mmol 1,2-*trans*-cyclohexanediol or 1,2-*trans*-diaminocyclohexane, 1.1 mL (8 mmol) of Et_3N, 4 mL of dry CH_2Cl_2 and 3 mg of 4-dimethylaminopyridine. The mixture was stirred for 12h at room temperature. It was diluted with 70 mL of $CHCl_3$, washed with 2% HCl (30 mL), 5% $NaHCO_3$ (2 x 50 mL), water (2 x 50 mL), dried (Na_2SO_4), filtered, and the solvent was removed under vacuum. Purification was achieved by radial chromatography eluting the bis-*p*-acetoxycinnamates with 0.75-1% CH_3OH in CH_2Cl_2 and bis-*p*-acetoxycinnamamides with 2-3% CH_3OH in CH_2Cl_2.

Racemic 1,2-*trans*-cyclohexanediol-bis-*p*-acetoxycinnamate was synthesized in 83% yield as an amorphous mass. ^{1}H-NMR: δ 1.50 (m, 4H), 1.80 (m, 2H), 2.15 (m, 2H), 2.26 (s, 6H), 5.03 (m, 2H), 6.33 (d, 2H, J=15.9 Hz), 7.08 (d, 4H, J=8.7 Hz), 7.49 (d, 4H, J=8.7 Hz), 7.61 (d, 2H, J=15.9 Hz) ppm; ^{13}C-NMR: δ 21.12, 23.53, 30.31, 73.98, 118.21, 122.04, 129.22, 132.04, 143.82, 152.00, 166.26, 169.10 ppm.

Anal. Calcd. for $C_{28}H_{28}O_8$ (492.5): C, 68.28; H, 5.73
Found: C, 68.12; H, 5.72

Racemic 1,2-*trans*-diaminocyclohexane-bis-*p*-acetoxycinnamamide was obtained in 73%. It had mp 288-289°C (CH_3OH/CH_2Cl_2). ^{1}H-NMR: δ 1.31 (m, 4H), 1.74 (m, 2H), 2.14 (m, 2H), 2.29 (s, 6H), 3.83 (m, 2H), 6.36 (d, 2H, J=15.6 Hz), 6.74 (shifted to 7.11 in concentrated solution) (d, 2H, J=7.0 Hz), 7.02 (d, 4H, J=8.6 Hz), 7.44 (d, 4H, J=8.6 Hz), 7.52 (d, 2H, J=15.6 Hz) ppm; ^{13}C-NMR: δ 21.10, 24.59, 31.98, 54.39, 120.94, 121.93, 128.88, 132.37, 139.88, 151.51, 166.82, 169.16 ppm.

Anal. Calcd. for $C_{28}H_{30}N_2O_6$ (490.5): C, 68.55; H, 6.16; N, 5.71
Found: C, 68.27; H, 6.31; N, 5.57

(+)-(1*S*,2*S*)-Cyclohexanediol-bis-*p*-acetoxycinnamate (5) was obtained in 91% yield as an amorphous mass. It had $[\alpha]_D^{20}$= +236.0 (c 1.2, CH_3OH) and ^{1}H- and ^{13}C-NMR were identical to those of racemic compound.

(+)-(1*S*,2*S*)-Diaminocyclohexane-bis-*p*-acetoxycinnamamide (6) was synthesized in 83% yield. It had mp 297-299°C (CH_3OH/CH_2Cl_2), $[\alpha]_D^{20}$= +213.6 (*c* 0.1, CH_3OH). Its ^{1}H- and ^{13}C-NMR spectra were the same as reported above for the racemic compound.

(−)-(1*R*,2*R*)-Cyclohexanediol-bis-*p*-acetoxycinnamate (**7**) was obtained in 90% yield as an amorphous mass. It had $[\alpha]_D^{20}$= −236.9 (c 1.9, CH_3OH). Its ^1H- and ^{13}C-NMR spectra were identical to those of racemic compound.

(−)-(1*R*,2*R*)-Diaminocyclohexane-bis-*p*-acetoxycinnamamide (**8**) was obtained in 89% yield. It had mp 297-299°C (CH_3OH/CH_2Cl_2), $[\alpha]_D^{20}$= −211.1 (c 0.1, CH_3OH). Its ^1H- and ^{13}C-NMR spectra were the same as reported above for the racemic compound.

***p*-Acetoxycinnamic acid cyclohexylamide** (**9**) was prepared in 93% yield. It had mp 194-195°C. ^1H-NMR: δ 1.18 (m, 4H), 1.39 (m, 2H), 1.72 (m, 2H), 1.98 (m, 2H), 2.31 (s, 3H), 3.91 (m, 1H), 5.51 (shifted to 6.95 in concentrated solution) (br.d, 1H, J=7.7 Hz), 6.30 (d, 1H, J=15.6 Hz), 7.08 (d, 2H, J=8.6 Hz), 7.49 (d, 2H, J=8.6 Hz), 7.58 (d, 1H, J=15.6 Hz) ppm; ^{13}C-NMR: δ 21.11, 24.83, 25.49, 33.15, 48.34, 121.33, 121.91, 128.74, 132.68, 139.45, 151.37, 164.69, 169.26 ppm.

General procedure for selective cleavage of the acetyl protecting group. To a solution of 0.25 mmol diacetyl derivative (**5-8**) in 3 mL of $CHCl_3$ (and 0.5-1 mL of CH_3OH to dissolve completely **6** and **8**) was added 0.75 mL (0.75 mmol) of 1 M CH_3ONa in CH_3OH (freshly prepared from Na) and stirred for 30 min.

The reaction mixtures containing bis-cinnamates (**1** and **3**) were diluted with 20 mL of $CHCl_3$ and stirred vigorously with 20 mL of 2% HCl. The organic layer was washed with water until neutral, dried (Na_2SO_4), filtered and the solvent was evaporated under vacuum. The bis-cinnamates were purified by radial chromatography eluting with 3-5% CH_3OH in CH_2Cl_2.

The reaction mixtures containing bis-cinnamamides (**2** and **4**) were partially evaporated under vacuum to remove CH_2Cl_2. The residue was diluted with 2 mL of CH_3OH and acidified with 10% HCl. Water was added dropwise (~10 mL) to precipitate the product. The bis-cinnamamides were purified by recrystallization from CH_3OH/Et_2O.

Racemic 1,2-*trans*-cyclohexanediol-bis-*p*-hydroxycinnamate was prepared in 75% yield as amorphous flakes. ^1H-NMR: δ 1.39 (m, 4H), 1.52 (m, 2H), 2.12 (m, 2H), 5.05 (m, 2H), 6.16 (d, 2H, J=15.9 Hz), 6.78 (d, 4H, J=8.8 Hz), 7.24 (d, 4H, J=8.8 Hz), 7.53 (d, 2H, J=15.9 Hz) ppm; ^{13}C-NMR: δ 23.58, 30.42, 74.44, 114.48, 115.93, 126.35, 130.18, 145.70, 158.57, 167.90 ppm.

Racemic 1,2-*trans*-diaminocyclohexane-bis-*p*-hydroxycinnamamide was obtained in 69% yield. It had mp 300-302°C (decomp.). ^1H-NMR ($(CD_3)_2SO$): δ 1.24 (br.m, 4H), 1.66 (br.m, 2H), 1.90 (br.m, 2H), 3.68 (br.m, 2H), 6.35 (d, 2H, J=15.9 Hz), 6.75 (d, 4H, J=8.4 Hz), 7.25 (d, 2H, J=15.9 Hz), 7.33 (d, 4H, J=8.4 Hz), 7.84 (br.d, 2H, J=6.1 Hz), 9.80 (s, 2H) ppm; ^{13}C-NMR ($(CD_3)_2SO$): δ 24.44, 32.21, 52.04, 115.72, 118.99, 125.91, 129.19, 138.56, 158.77, 165.30 ppm.

(+)-(1*S*,2*S*)-Cyclohexanediol-bis-*p*-hydroxycinnamate (**1**) was prepared in 65% yield as amorphous flakes. It had $[\alpha]_D^{20}$= +397.3 (*c* 1.1, CH_3OH) and ^1H- and ^{13}C-NMR spectra were identical to those of racemic compound.

Anal. Calcd. for $C_{24}H_{24}O_6 \cdot 1/2\ CH_3OH$ (424.5): C, 69.32; H, 6.17
Found: C, 69.49; H, 5.87

(+)-(1*S*,2*S*)-Diaminocyclohexane-bis-*p*-hydroxycinnamamide (2) was obtained in 88% yield. It had mp 304-306°C (decomp.), $[\alpha]_D^{20}$= +337.4 (*c* 0.8, CH_3OH). Its ^1H- and ^{13}C-NMR spectra were the same as reported above for the racemic compound.

Anal. Calcd. for $C_{24}H_{26}N_2O_4$ (406.5): C, 70.91; H, 6.45; N, 6.89
Found: C, 70.64; H, 6.47; N, 6.82

(−)-(1*R*,2*R*)-Cyclohexanediol-bis-*p*-hydroxycinnamate (3) was prepared in 77% yield as amorphous flakes. It had $[\alpha]_D^{20}$= −399.3 (*c* 1.0, CH_3OH). Its ^1H- and ^{13}C-NMR spectra were identical to those of racemic compound.

(−)-(1*R*,2*R*)-Diaminocyclohexane-bis-*p*-hydroxycinnamamide (4) was obtained in 84% yield. It had mp 304-306°C (decomp.), $[\alpha]_D^{20}$= −338.9 (*c* 1.3, CH_3OH). Its ^1H- and ^{13}C-NMR spectra were the same as reported above for the racemic compound.

***p*-Hydroxycinnamic acid cyclohexylamide (10)** was prepared in 81% yield. It had mp 195-197°C (decomp.) ^1H-NMR ($(CD_3)_2SO$): δ 1.22 (m, 6H), 1.67 (m, 2H), 1.75 (m, 2H), 3.62 (m, 1H), 6.39 (d, 1H, J=15.7 Hz), 6.76 (d, 2H, J=8.3 Hz), 7.28 (d, 1H, J=15.7 Hz), 7.35 (d, 2H, J=8.3 Hz), 7.84 (d, 1H, J=7.9 Hz), 9.81 (s, 1H) ppm; ^{13}C-NMR ($(CD_3)_2SO$): δ 24.64, 25.31, 32.64, 47.50, 115.76, 119.07, 126.05, 129.14, 138.51, 158.78, 164.42.

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