37, 45, 50, and 60 °C for the decomposition of **47** are given in Table IV.

DNA Cleavage. All DNA cleavage experiments were performed with ΦX174 DNA (50 μM/base pair) in a pH 8.5 Tris-acetate buffer (50 mM). The results were analyzed using 1% agarose gel electrophoresis and detection with ethidium bromide fluorescence. Figure 2 shows the pictures of the agarose gel electrophesis results.

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Determination of the Absolute Stereochemistry of Nemadectins α_2 and α

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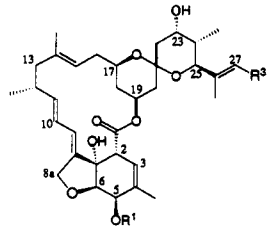
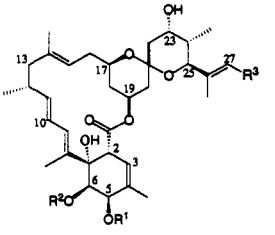
Abstract: The CD exciton chirality method has been applied to determine the absolute configuration of the nemadectins (formerly LL-F28249 series). The CD spectra of the 5-benzoates **6** and **7** of nemadectins α (**1**) and α_2 (**5**), respectively, show that both have *R* configurations at C-5. Furthermore, what appears to be the short-wavelength wing of a split CD due to an exciton-coupled allylic benzoate system has been observed for the first time at ca. 190 nm. The CD of the 5,6-bis(*p*-methoxycinnamate) 23-acetate (**9**) of nemadectin α_2 also shows that the C-5 and C-6 configurations are both *R*. The consistent results from both approaches establish the absolute configuration of this important group of antiparasitic agents.

Introduction

Nemadectins represent a new family of macrocyclic lactones possessing potent antiparasitic activity against a broad spectrum of endo- and ectoparasites of mammals. Isolation and structures of the four principal nemadectins, α (**1**), β (**2**), λ (**3**), and γ (**4**), were reported previously.[1,2] The nemadectins are distinguished





(1) R^1 = H, R^3 = *i*-Pr (α)
(2) R^1 = H, R^3 = Me (β)
(3) R^1 = Me, R^3 = *i*-Pr (λ)
(4) R^1 = Me, R^3 = Me (γ)
(5) R^1 = H, R^2 = H, R^3 = *i*-Pr (α_2)
(6) R^1 = Bz, R^3 = *i*-Pr
(7) R^1 = Bz, R^2 = H, R^3 = *i*-Pr
(9) R^1 = R^2 = *p*-MeO-Cn, R^3 = *i*-Pr (-OAc instead of -OH at C-23)

from the avermectins[3] and the milbemycins[4] by the presence of unsaturated side chains at C-25 and by the hydroxyl group at C-23. Nemadectin α differs from nemadectin β by having an isopropyl rather than a methyl group at C-27, while nemadectin λ and nemadectin γ are their respective 5-methoxy derivatives. The main congener, nemadectin α, is currently used as starting material for the production of commercial moxidectin (Cydectin) used in veterinary medicine.

Extracts from fermentation broths of *Streptomyces cyaneogriseus* ssp. *noncyanogenus* contain numerous nemadectins, most of which have been isolated and characterized.[5] Of these, we have selected nemadectins α and α_2 (**1** and **5**) for absolute configurational studies by the CD exciton chirality method.[6] The conformation and relative configuration of nemadectin α_2 have also been determined by X-ray crystallography.

Results and Discussion

The structures of nemadectins α and α_2 suggest the possibility of applying two different approaches in the exciton chirality method for elucidation of the absolute stereochemistry, namely, the allylic benzoate method[7] to the allylic alcohol systems composed of the 3-ene/5-hydroxyl in α and α_2 and the biscinnamate method[8] to the 5,6-glycol moiety in nemadectin α_2. In the allylic benzoate method, it has been demonstrated that (i) in both cyclic[7a] and acyclic systems,[7b] the long-axis π-π* electric transition moment

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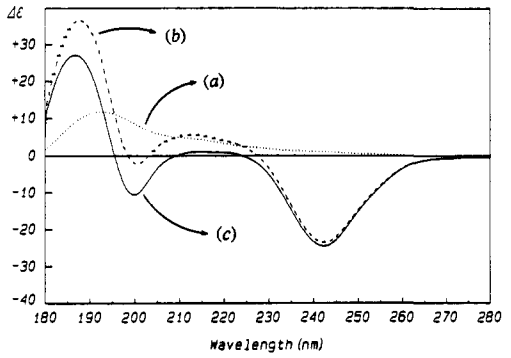


Figure 1. CD spectra (in TFE) of (a) nemadectin α_2 (**5**), (b) 5-benzoate **7**, and (c) the difference spectrum of **5** and **7**.

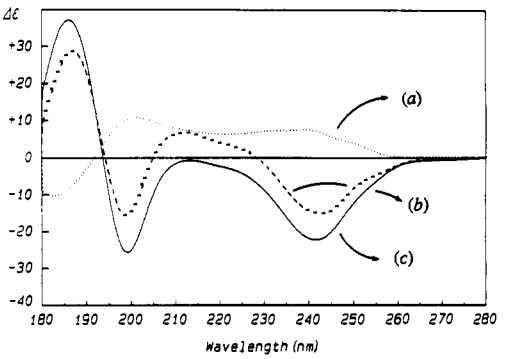
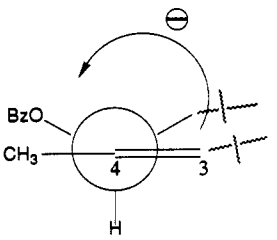


Figure 2. CD spectra (in TFE) of (a) nemadectin α (**1**), (b) 5-benzoate **6**, and (c) the difference spectrum of **1** and **6**.

of the benzoate chromophore interacts with the π–π^* transition of the allylic double bond at ca. 190 nm to give rise to chiral exciton coupling; and (ii) although the shorter wavelength wing of the corresponding CD Cotton effect (CE) cannot be measured or overlaps with other transitions, the sign of the readily detectable longer wavelength counterpart correctly represents the chirality of the allylic alcohol moiety. Both measurements led to the same absolute stereochemistry for nemadectins α and α_2.

Allylic Benzoate Chiral Exciton Coupling. A. 5-Monobenzoate of Nemadectin α_2 (7). The 5-monobenzoate (**7**) of nemadectin α_2 is readily prepared by virtue of the higher reactivity of 5-OH. The derivatization at C-5 is evidenced by the ^{1}H NMR data with the C-5 proton shifting from 4.42 to 6.20–6.00 ppm in the case of α_2 and from 4.29 to 5.80–5.63 ppm for nemadectin α. The CD spectrum of nemadectin α_2 (in trifluoroethanol, Figure 1, curve a) exhibits the following CEs: 235 ($\Delta\epsilon$ +1.3, diene), 212 (+4.7, lactone), and 192 nm (+11.7, composite of various transitions); note that the CE around 235 nm arising from the diene moiety is quite weak. Benzoate **7** absorbs at an unusually long wavelength of 238 nm (in TFE) as compared to the usual maximum at ca. 230 nm;[9] its CD spectrum (Figure 1, curve b) exhibits extrema at 243 ($\Delta\epsilon$ −23.5, benzoate CE overlapping with weak diene CE), 213 (+5.5), 200 (−2.2), and 188 nm (+36.6) (see below for comments). The difference CD spectrum (Figure 1, curve c) of nemadectin α_2 and its 5-benzoate (**7**) shows a clearly negative CE around 243 nm, thus indicating that the 5-benzoate group and the allylic 3-ene constitute a negative exciton chirality (**8**);[7] this leads to a 5*R* configuration and thus to structure **5** for nemadectin α_2 as depicted.



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B. 5-Monobenzoate of Nemadectin α (6). This allylic benzoate couplet was also measured for the 5-benzoate (**6**) of nemadectin α. The CD of nemadectin α (TFE, Figure 2, curve a) shows CEs at 239 ($\Delta\epsilon$ +7.5, diene), 201 (+10.7, lactone), and 183 nm (−10.2). The diene CE at ca. 240 nm for α, which is 6-fold more intense than that of α_2 (due to differences in chiral environment), exhibits fine structure at 249, 239, and 230 nm. This reflects the higher rigidity in α as evidenced by enhanced UV vibrational structure (relative to α_2) at 252, 242, and 233 nm (TFE);[10] the interval of 1600 cm^{-1} corresponds to vibrational frequencies of C=C double bonds. The CD of the 5-benzoate (**6**) (Figure 2, curve b) has the following extrema: 243 ($\Delta\epsilon$ −15.0, benzoate and diene), 211 (+6.7, lactone), 199 (−15.6, mostly benzoate B transition?), and 187 nm (+28.7); UV λ_{max} (TFE) broad between 237 and 242 nm. The difference CD spectrum (Figure 2, curve c) of nemadectin α and its 5-benzoate **6** again shows a strong negative CE at ca. 240 nm, indicating that the sense of screwness between the 3-ene and the 5-benzoate long-axis transition moment is negative, i.e., 5*R* absolute configuration. It is likely that the strongly positive maximum at ca. 187 nm in the CD spectra of benzoates **6** and **7** is the shorter wavelength counterpart of the 3-ene/5-benzoate exciton couplet; if so, it would be the first experimental observation of both wings of an allylic benzoate couplet. This aspect is the subject of future studies in the region below 200 nm. Thus, both 5-benzoates **6** and **7** lead to the depicted absolute configurational structure for nemadectins α and α_2.

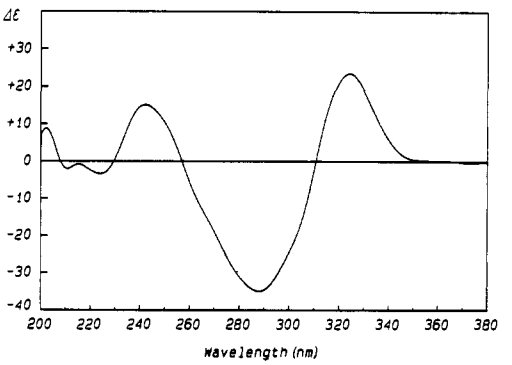

Figure 3. CD spectrum of the 5,6-bis(*p*-methoxycinnamate) 23-acetate of nemadectin α_2 (**9**) in acetonitrile.

Biscinnamate Chiral Exciton Coupling. 5,6-Bis(*p*-methoxycinnamate) 23-Acetate of α_2 (9). The *p*-methoxycinnamate chromophore was used because of its high UV ϵ value of 24 000 and because its λ_{max} of 311 nm[8] is remote from that of α_2 (λ_{max} 242 nm); the resulting split CD can thus be attributed to the coupling between vicinal cinnamates at C-5 and C-6 without interference from the existing chromophores in the molecule.

The CD spectrum of the biscinnamate (**9**) of nemadectin α_2 shows a strong, positively split CD band with extreme at 324 (+24.4) and 288 nm (−36.3),[11] with an *A* value of +60.7 (in acetonitrile) (Figure 3). This strong coupling arising from the cinnamate–cinnamate interaction indicates that the two chromophores constitute a clockwise exciton chirality. However, application of this result to the determination of absolute configuration requires knowledge of the preferred conformation of the cyclohexene ring, namely, if the ring adopts the half-chair

(9) Chapter 7-4 of ref 6, pp 260–272.

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(11) The $\Delta\epsilon$ of this negative wing is stronger than that of the positive counterpart at 324 nm, which implies that some other exciton interactions must have also contributed besides the major cinnamate–cinnamate interaction. These additional contributions include 5-cinnamate/3-ene and 6-cinnamate/8,9,10,11-diene interactions, both having negative signs at around 288 nm.

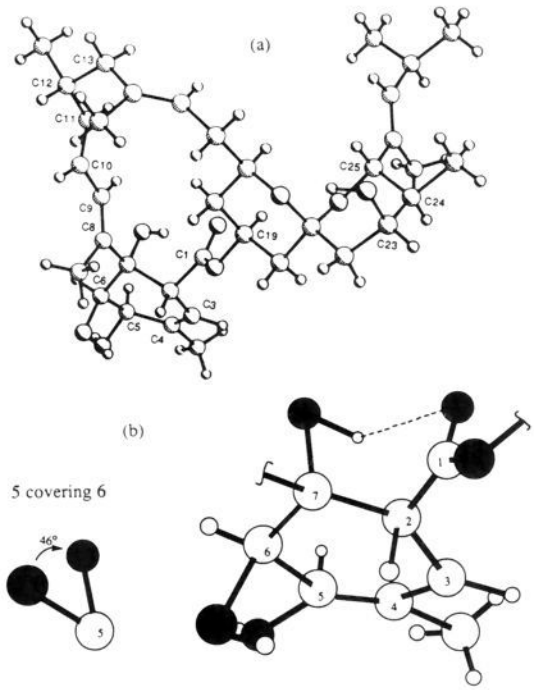
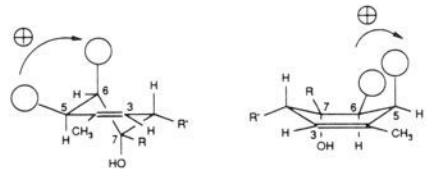


Figure 4. PLUTO representation (a) and partial structure (b) of nemadectin α_2 (**5**).

conformation **9a**, the absolute configurations will be 5*R*,6*R*, whereas if it adopts the half-boat conformation **9b**, the configurations will be 5*S*,6*S*. In both cases, the cinnamate–cinnamate interaction would lead to a positively split CD.



9a *(5R,6R)* **9b** *(5S,6S)*

The preferred conformation of the cyclohexene ring in solution, as determined by NOE studies, was compared with its solid-state conformation established by single-crystal X-ray diffraction analysis of nemadectin α_2. The X-ray structure shows that the cyclohexene ring adopts the half-chair conformation (Figure 4). Molecular models of the 5,6-biscinnamate **9** indicate that the half-chair conformation **9a** would result in nearly equivalent NOEs for 7-OH/5-H and 7-OH/6-H, whereas the half-boat conformation **9b** would result in a much larger NOE for 7-OH/6-H than for 7-OH/5-H. The experiments indicate that 7-OH/5-H and 7-OH/6-H exhibit weak but similar NOE values of 1% in $CDCl_3$; this leads to the conclusion that the biscinnamate adopts the half-chair conformation **9a** (probably in acetonitrile as well as in $CDCl_3$). Therefore, the absolute configurations of nemadectin α_2 at C-5 and C-6 should be 5*R* and 6*R*. This is in agreement with the results obtained from the allylic benzoate method.

Conclusion

Single-crystal X-ray diffraction analysis for nemadectin α_2 established that the relative stereochemistry is the same as previously demonstrated for nemadectin γ^1 and the avermectins,[3] while the same relative stereochemistry was assigned to nemadectin α by correlation of NMR data. The absolute configurations at C-5 and C-6 of nemadectins α and α_2 were determined to be 5*R* and 6*R*, namely, the absolute configuration at C-5 of both nemadectin α and α_2 was derived from the sign of the CE of their allylic 5-benzoates to be *R*. Furthermore, what seems to be the short-wavelength wing of an exciton-coupled allylic benzoate system has been recorded for the first time. For nemadectin α_2, the absolute configurations at C-5 and C-6 were derived independently by CD analysis and NOE studies of its 5,6-bis(*p*-methoxycinnamate) derivative.

With the relative stereochemistry of nemadectins α and α_2 established and the absolute configurations at C-5 and C-6 determined, the absolute configurations of the 11 chiral centers of the nemadectins are assigned as follows: 2*R*, 5*R*, 6*R*, 7*S*, 12*R*, 17*R*, 19*S*, 21*R*, 23*S*, 24*S*, and 25*S*. The absolute configuration at C-12 is *R* for the nemadectins, whereas it is *S* for the avermectin series due to reversed priorities in the sequence rule[12] at the oxygen-bearing moieties at C-13. The absolute stereochemistry of the nemadectins is thus identical to that of the avermectins[3] and the milbemycins.[4]

Experimental Section

Materials. THF, chloroform, ethyl acetate, and hexane (all HPLC grade) were purchased from Fisher. Acetonitrile (HPLC grade), trifluoroethanol (NMR grade), (dimethylamino)pyridine (DMAP), and dimethoxypropane were purchased from Aldrich. Pyridine was distilled from CaH_2. *p*-Methoxycinnamoyl chloride was prepared as described previously.[8b] Silver triflate (from Aldrich) was dried by several evaporations on a rotary evaporator with benzene in the dark followed by pumping under high vacuum. Thin-layer chromatography was performed with silica gel 60F 254 glass plates of 0.25 mm thickness from E. Merck.

Instrumentation. CD spectra (λ_{ext} (nm)/$\Delta\epsilon$) were measured with a JASCO J-720 spectropolarimeter in either trifluoroethanol (TFE) or acetonitrile. Smoothing and mathematical manipulations were carried out using software developed in house. ^{1}H NMR spectra were obtained with a Varian VXR (400 MHz), a GE QE+ (300 MHz), or a Bruker WM (250 MHz) spectrometer as noted. Chemical shifts were determined in parts per million relative to the solvent signal of deuteriochloroform at δ 7.24 and at δ 77.0 ppm for ^{1}H and ^{13}C NMR spectra, respectively. UV spectra were obtained on a Perkin-Elmer Lambda 4B UV/vis spectrophotometer. Low-resolution mass spectroscopy was measured on a JEOL JMS-DX303HF mass spectrometer.

X-ray Analysis. Nemadectin α_2 crystallized from an acetonitrile–water solution in colorless, prism-shaped needles (mp 220–223 °C). A crystal having the approximate dimensions 0.12 × 0.07 × 0.04 mm was selected for X-ray diffraction. Crystal survey, unit cell determination, and data collection were performed using copper radiation at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares and difference Fourier methods. Two unique molecules were found to form an asymmetric ($P1$) unit cell with a = 11.074 (1), b = 15.7341 (8), c = 10.690 (1) Å, and V = 1830.6 (3) Å^3. For Z = 2 and FW = 614.82, the calculated density is 1.115 g/cm^3. Of the 4027 reflections collected, 3771 were unique ($R_{int.}$ = 0.015). The intensities of the three representative reflections that were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability.

Isolation of Nemadectin α_2 (5). The nemadectin complex was extracted from fermentation broths as described previously.[2] Nemadectin α_2 coeluted with α during chromatography on silica gel, but was subsequently separated from α by reversed-phase chromatographies on a Whatman CCS/C_8 column using 80% MeOH in H_2O first and on rechromatography of the α_2-cut, 70% acetonitrile in H_2O as the mobile phase. Nemadectin α_2 crystallized from the aqueous acetonitrile solution (mp 220–223 °C): ^{13}C NMR (75 MHz, $CDCl_3$) 174.6, 140.8, 137.3, 136.8, 136.2, 136.1, 130.4, 126.1, 124.2, 120.4, 118.0, 99.7, 77.8, 76.7, 72.7, 69.8, 69.3, 68.4, 67.3, 48.6, 44.3, 41.1, 40.4, 36.0, 35.9, 34.7, 34.4, 26.8, 22.8, 22.7, 20.6, 19.2, 15.9, 13.9, 13.6, 10.9; ^{1}H NMR (300 MHz, $CDCl_3$) 6.10, 6.08 (dd, 2 H, J = 15.0, 11.2 Hz), 5.39 (dd, 1 H, J = 10.6, 15.0 Hz), 5.36 (m, 1 H), 5.27 (d, 1 H, J = 1.5 Hz), 5.14 (dd, 1 H, J = 8.8, 1.3 Hz), 4.83 (m, 1 H), 4.42 (d, 1 H, J = 4.0 Hz, H-5), 3.89 (s, 1 H), 3.83 (d, 1 H, J = 4.0 Hz), 3.79 (m, 1 H), 3.74 (m, 1 H), 3.69 (d, 1 H, J = 10.6 Hz), 3.67 (m, 1 H), 3.64 (d, 1 H, J = 10.1 Hz), 2.52 (m, 1 H), 2.45 (m, 1 H), 2.3–1.5 (m, 12 H), 1.90 (s, 3 H), 1.80 (d, 3 H, J = 1.5 Hz), 1.61 (s, 3 H), 1.54 (s, 3 H), 1.03 (d, 3 H, J = 6.6 Hz), 0.99 (d, 3 H, J = 6.6 Hz), 0.90 (d, 3 H, J = 6.6 Hz), 0.85 (dd, 1 H, J = 12.2 Hz), 0.76 (d, 3 H, J = 6.9 Hz); negative thermospray MS 614 (58, $[M]^-$), 597 (100, $[M - OH]^-$); CD of nemadectin α_2 (TFE) 235 sh (+1.3), 212 sh (+4.7), 192 (+11.7); CD of nemadectin α^1 (TFE) 249 sh (+4.3), 239 (+7.5), 201 (+10.7), 183 (−10.2).

5-Benzoate of Nemadectin α_2 (7). Benzoyl chloride (2 μL) was added to the solution of 7.0 mg of nemadectin α_2 with a catalytic amount of DMAP in 250 μL of anhydrous pyridine at 0 °C. The solution was

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stirred overnight at room temperature. One drop of water was then added to quench the reaction. The reaction mixture was filtered through a short pipet packed with basic alumina, washed with AcOEt, and concentrated to dryness. TLC shows a major spot (R_f 0.45, AcOEt/hex = 1/2) and a minor one (R_f 0.62, AcOEt/hex = 1/2). The mixture was then purified with preparative TLC, and the desired product **7** was recovered (8.0 mg). The NMR spectrum indicates that it is monobenzoylated at C-5. Data for **7**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (d, J = 7.3 Hz, 2 H), 7.57 (dd, J = 7.3, 7.8 Hz, 1 H), 7.44 (dd, J = 7.3, 7.8 Hz, 2 H), 6.20–6.00 (3 H), 5.46 (d, 1 H, J = 1.6 Hz), 5.43–5.32 (2 H), 5.14 (d, 1 H, J = 9.1 Hz), 4.84 (1 H), 4.13 (dd, 1 H, J = 3.0, 3.1 Hz), 3.95 (s, 1 H), 3.85 (d, 1 H, J = 3.9 Hz), 3.79 (dd, 1 H, J = 10.1, 2.4 Hz), 3.76–3.63 (m, 2 H), 3.59 (d, 1 H, J = 10.1 Hz), 2.61–2.38 (m, 2 H), 2.34–1.45 (m, 24 H), 1.03 (d, 3 H, J = 6.7 Hz), 1.00 (d, 3 H, J = 6.7 Hz), 0.91 (d, 3 H, J = 6.6 Hz), 0.77 (d, 3 H, J = 7.0 Hz); FAB-MS 719 (11, $[M + H]^+$), 701 (28, $[M - OH]^+$); CD (TFE) 243 (−23.5), 213 (+5.5), 202 (−2.2), 188 (+36.6).

5-Benzoate of Nemadectin α (6). Benzoyl chloride (4 μL) was added to a solution of 11.6 mg of nemadectin α^1 in 500 μL of anhydrous pyridine at 0 °C. The solution was stirred overnight at room temperature. The reaction was worked up as above. The desired product **6** (6.0 mg) was purified with preparative TLC (R_f 0.44, AcOEt/hex = 1/2). The NMR spectrum indicates that it is monobenzoylated at C-5. Data for **6**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.07 (d, 2 H, J = 7.1 Hz), 7.56 (dd, 1 H, J = 7.8, 7.1 Hz); 7.43 (dd, 2 H, J = 7.8, 7.1 Hz), 5.80–5.63 (3 H), 5.57 (d, 1 H, J = 1.5 Hz), 5.40–5.25 (2 H), 5.20 (d, 1 H), 4.95 (m, 1 H), 4.63 (dd, 1 H, J = 13.4, 1.9 Hz), 4.53 (dd, 1 H, J = 13.4, 1.9 Hz), 4.18 (d, 1 H, J = 5.9 Hz), 3.84–3.53 (m, 5 H), 3.38 (dd, 1 H, J = 4.7, 2.3 Hz), 2.58 (m, 1 H), 2.39 (m, 1 H), 2.32–1.33 (m, 20 H), 1.04 (d, 3 H, J = 7.7 Hz), 0.97 (d, 3 H, J = 6.6 Hz), 0.94 (d, 3 H, J = 7.7 Hz), 0.78 (d, 3 H, J = 6.9 Hz); FAB-MS 717 (13, $[M + H]^+$), 699 (36, $[M - OH]^+$); CD (TFE) 253 sh (−5.6), 243 (−15.0), 211 (+6.7), 199 (−15.6), 187 (+28.7).

5,6-Bis(*p*-methoxycinnamate) 23-Acetate of Nemadectin α_2 (9). (a) Acetonide Formation of Nemadectin α_2. A total of 9.0 mg of nemadectin α_2 was dissolved in 1 mL of $Me_2C(OMe)_2$, and a catalytic amount of TsOH was added. After 2 h the reaction mixture was diluted with 4 mL of Et_2O and passed through a short column packed with basic alumina then washed with 5 mL of AcOEt. The eluent was evaporated to dryness. The acetonide (R_f 0.76, AcOEt/hex = 1/2) was used for the next step without further purification.

(b) Acetylation of the Acetonide. To the above product were added 100 μL of Ac_2O, 300 μL of pyridine, and a catalytic amount of DMAP. The reaction mixture was stirred at room temperature for 14 h and then concentrated to dryness. The acetylated product (8.9 mg) was purified with preparative TLC (R_f 0.78, AcOEt/hex = 1/2): ^{1}H NMR (250 MHz, $CDCl_3$) 6.23 (d, 1 H, J = 10.8 Hz), 6.06 (dd, 1 H, J = 14.7, 10.8 Hz), 5.44–5.10 (m, 4 H), 4.94–4.75 (m, 2 H), 4.46 (d, 1 H, J = 4.2 Hz), 4.00 (d, 1 H, J = 4.9 Hz), 3.88 (d, 1 H, J = 10.4 Hz), 3.76 (s, 1 H), 3.70–3.51 (m, 2 H), 2.63–1.20 (m, 34 H), 1.10–0.62 (m, 12 H); FAB-MS 719 (4, $[M + Na]^+$), 697 (6, $[M + H]^+$), 679 (6, $[M - OH]^+$).

(c) Deprotection of the Acetonide. To the above product was added 2 mL of THF–1 N HCl (1/1). The reaction mixture was stirred at 50 °C for 8 h. The reaction was not complete as monitored with TLC. There were two major spots with R_f values of 0.78 (starting material) and 0.33, respectively. The lower spot was the deprotected product and was collected (2.2 mg): ^{1}H NMR (250 MHz, $CDCl_3$) 6.21–6.02 (m, 2 H), 5.53–5.26 (m, 3 H), 5.16 (d, 1 H, J = 8.7 Hz), 4.98–4.88 (m, 2 H), 4.48 (s, 1 H), 4.05–3.55 (m, 6 H), 2.66–1.38 (m, 29 H), 1.18–0.62 (m, 12 H).

(d) para-Methoxycinnamoylation. A total of 10 mg of *p*-methoxycinnamoyl chloride, 10 mg of AgOTf, and a catalytic amount of DMAP were added to the solution of 2.2 mg of the above product in 400 μL of anhydrous pyridine. The mixture was stirred at room temperature for 20 h and then worked up as for benzoylation. The biscinnamate **9** was purified with preparative TLC (R_f 0.44, AcOEt/hex = 1/2): ^{1}H NMR (400 MHz, $CDCl_3$) 7.56 (d, 1 H, J = 15.9 Hz), 7.53 (d, 1 H, J = 16.0 Hz), 7.45 (d, 2 H, J = 8.7 Hz), 7.31 (d, 2 H, J = 7.8 Hz), 6.88 (d, 2 H, J = 8.7 Hz), 6.77 (d, 2 H, J = 7.8 Hz), 6.31 (d, 1 H, J = 16.0 Hz), 6.18 (d, 1 H, J = 15.9 Hz), 6.11–5.94 (m, 3 H), 5.56 (d, 1 H, J = 4.0 Hz), 5.50–5.33 (m, 3 H), 5.16 (d, 1 H, J = 9.1 Hz), 4.93–4.89 (m, 2 H), 4.18 (s, 1 H), 3.95–3.70 (m, 9 H), 3.62 (m, 1 H), 2.53 (m, 1 H), 2.41 (m, 1 H), 2.32–1.38 (m, 25 H), 1.00 (m, 6 H), 0.91 (d, 3 H, J = 6.7 Hz), 0.68 (d, 3 H, J = 6.8 Hz); FAB-MS 977 (13, $[M + H]^+$), 959 (67, $[M - OH]^+$); CD (CH_3CN) 324 (+24.4), 288 (−36.3), 242 (+15.7).

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Supplementary Material Available: X-ray diffraction data including a description of experimental procedures, references, tables listing experimental details, positional and thermal parameters, temperature factors, bond distances, bond angles, torsional angles, intermolecular contacts up to 3.60 Å, and intensity data, and figures of PLUTO and ORTEP representations (69 pages); table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.