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Synthesis of Structurally Simplified Aureolic Acid Aglycone-C–D–E Trisaccharide Analogues

William R. Roush,[A,B] *Noel A. Powell*[A] *and Ray A. James*[A]

[A] Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, U.S.A.
[B] Author to whom correspondence should be addressed (e-mail: roush@umich.edu).

Syntheses of aureolic acid analogues (5) and (6) with (2*S*)- and (2*R*)-acyloin stereochemistry, respectively, are described. The synthesis of (5) utilizes a 'C + DE' glycosidation sequence, whereas analogue (6), with unnatural (2*R*)-acyloin stereochemistry, was synthesized by a sequence in which the entire C–D–E trisaccharide was introduced in a single step. While these syntheses provided sufficient quantities of the two aureolic acid analogues for use in studies of Mg^{2+} complex formation and deoxyribonucleic acid (DNA) binding, this work also highlights certain limitations in the use of 2-thiophenyl glycosyl donors for synthesis of 2-deoxy-β-glycosides. Specifically, difficulties were encountered in the identification of a protecting group for the aglycone C8 phenol that is fully compatible with the conditions required for reductive removal of the thiophenyl substituents after completion of the glycosidation sequence. Sensitivity of the C2 acyloin stereocentre to the conditions required for deprotection of a phenolic acetate ester are also highlighted in the syntheses of (5), and especially of (6).

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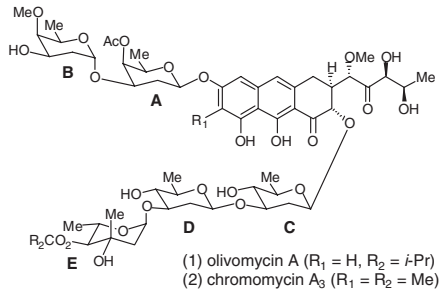
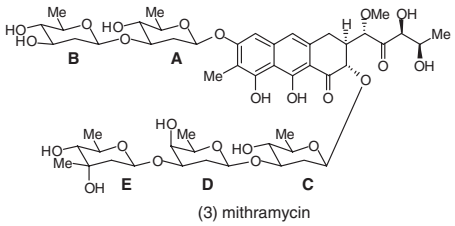
Introduction

Olivomycin A (1), chromomycin A_3 (2) and mithramycin (3) are well known members of the aureolic acid family of antitumour antibiotics.[1–3] Mithramycin (3) has been used clinically in the U.S. for treatment of testicular tumours, while chromomycin A_3 has been used in Japan in combination with mitomycin C and 5-fluorouracil for treatment of solid tumours, particularly advanced stomach cancers.[2] The aureolic acids are inhibitors of DNA-dependent ribonucleic acid (RNA) polymerase, and bind in the minor groove of double stranded DNA as 2:1 antibiotic/Mg^{2+} complexes with selectivity for guanine/cytosine (GC)-rich sequences.[4–7] Under certain conditions (low Mg^{2+} concentration), a 1:1 complex has also been detected.[8,9] Mithramycin binds to the GC-rich promoter regions of the c-myc protooncogene and the dihydrofolate-reductase gene, thereby preventing their translation.[10,11]





The aureolic acid antibiotics have attracted considerable attention in view of the role played by the oligosaccharide units in DNA binding, Mg^{2+} complex formation, and the biological manifestations of these properties.[12–17] Nuclear magnetic resonance (NMR) studies by Patel[4,5] and Kahne[13,14] have established that the C–D disaccharide of one monomer stacks on the aromatic nucleus of the other aglycone in the 2:1 complexes with Mg^{2+}, both when bound to DNA,[4,5] and when free in MeOH solution.[13,14] The intact C–D–E trisaccharide is essential for stable dimer formation (in MeOH)[13,14] and maximal DNA binding,[18,19] as well as for full activity as an antitumour agent.[1–3] However, the roles played by the A–B disaccharide and the C3 polyoxygenated side chain in the DNA binding event have not been delineated. Kahne has demonstrated that aureolic acid analogue (4), containing a triethylene glycol mimic of the C–D–E trisaccharide, forms a 2:1 complex with Mg^{2+}, but DNA-binding data have not been reported.[15,16]

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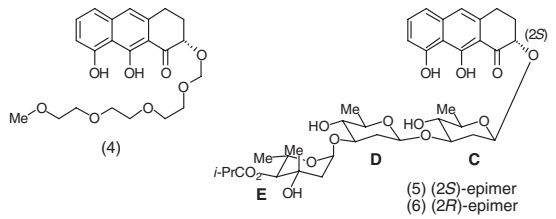
As part of a program aimed at defining the minimal structural requirements for DNA binding by the aureolic acid antibiotics, we targeted the synthesis of the simplified analogues (5) and (6) lacking the A–B disaccharide and C3 side chain. We report herein the syntheses of (5) and (6). Studies of Mg^{2+} complex formation and DNA-binding properties of these analogues are being performed in collaboration with Professor D. Kahne of Princeton University, and will be reported in due course.

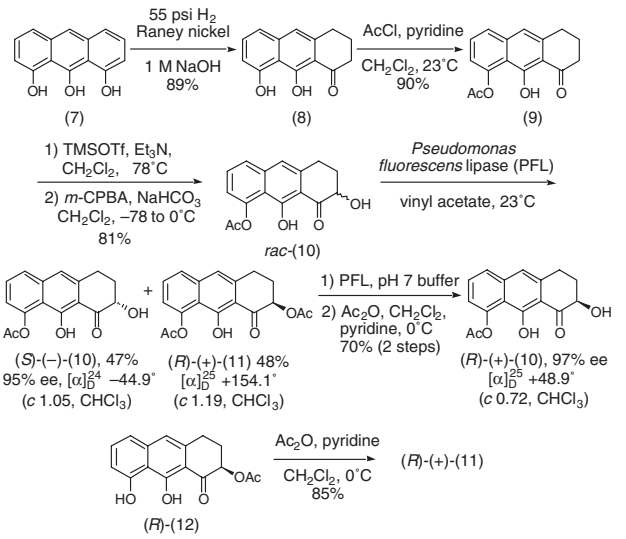


Results and Discussion

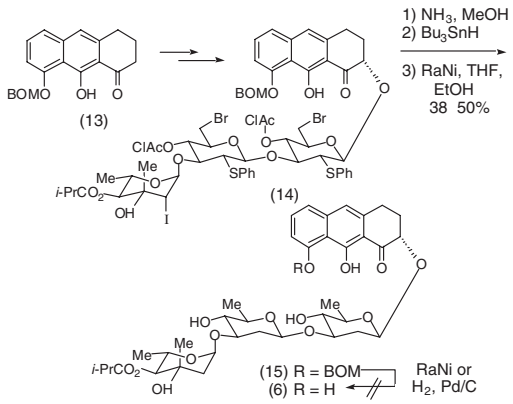
Synthesis of Analogue (5)

The aglycon unit of analogue (5) was synthesized from anthralin (7) by using modifications of the sequence reported by Kahne.[15,16] Raney nickel (RaNi) catalysed hydrogenation of (7) gave diphenolic ketone (8) (Scheme 1). We found it advantageous to protect the C8 phenol of (8) in order to improve the handling characteristics of the air- and acid-sensitive ketone and subsequent intermediates. In early stages of this work, we protected (8) as a benzyloxymethyl (BOM) ether [see (13), Scheme 2] and elaborated this intermediate to the protected trisaccharide conjugate (14) by using the glycosidation chemistry employed in our synthesis of olivomycin A.[20] However, while mild dechloroacetylation of (14) followed by Bu_3SnH reduction of the three halogen substituents and RaNi reduction of the two thiophenyl groups provided a route to (15), all attempts to remove the C8 BOM-ether protecting group by hydrogenation protocols were unsuccessful. Although we were able to obtain ^1H NMR and mass spectroscopic evidence for production of (6) in RaNi reductions of (15), mass recoveries were always extremely poor and we were never able to isolate research quantities of (6) with acceptable purity. We attributed these difficulties to the propensity of (6) to bind to metal ions (or surfaces). Similar issues were encountered in the final stages of our olivomycin A total synthesis,[20] a problem that we circumvented by adjusting the physical properties of the substrate for the RaNi reduction by incorporation of several silyl ether protecting groups earlier in the synthesis. Regrettably, similar tactics were not successful in our efforts to synthesize (6) from precursors (14) and (15).

After consideration of other protecting groups for the C8 phenolic unit, we settled on the use of an acetate ester for these purposes. Thus, acylation of (8) with acetyl chloride and pyridine provided monoacetate (9) in excellent yield (Scheme 1). This intermediate was readily converted into racemic α-hydroxy ketone (10) by Rubottom oxidation of

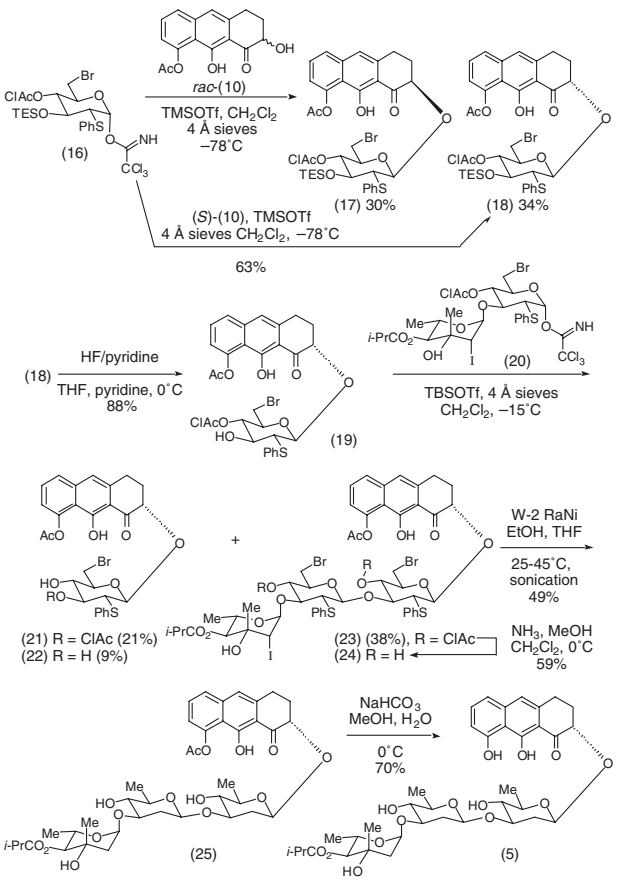


Scheme 1. Synthesis of glycosidation substrates (*S*)-(10) and (*R*)-(10).



Scheme 2. Synthesis of BOM-protected trisaccharide conjugate (15).

the intermediate enol silane.[21–23] Enzymatic resolution of racemic (10) using *Pseudomonas fluorescens* lipase (PFL) in vinyl acetate provided alcohol (*S*)-(10) and the enantiomeric diacetate (*R*)-(11) with almost perfect enantioselectivity.[15,16] Deacylation of (11) was performed using PFL in aqueous buffer to prevent racemization of the acyloin centre. However, under these conditions the C8 phenolic acetate was also hydrolysed.[24] The C8 acetate was easily reinstalled selectively by using Ac_2O and pyridine in CH_2Cl_2, thereby providing (*R*)-(10) in good overall yield with no loss of enantiomeric purity. The enantiomeric purity of alcohols (*S*)- and (*R*)-(10) was assessed by using the Mosher ester analysis,[25] and their absolute configurations were confirmed by conversion of (*R*)-(12), which was prepared by PFL-mediated resolution of the diphenol corresponding to *rac*-(10),[15,16] into the diacetate (*R*)-(11). It should be noted that the stereochemistry of these intermediates reflects the recently reassigned stereostructure of (*R*)-(12).[26]

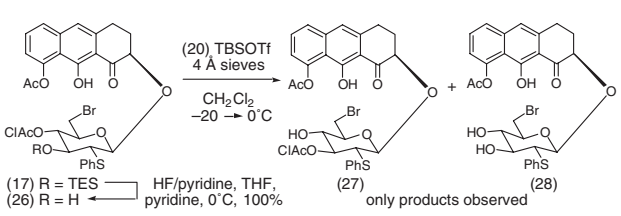


Scheme 3. Synthesis of aureolic acid analogue (5) with natural (2*S*)-acyloin stereochemistry.

Our synthesis of analogue (5) with the natural (2*S*)-stereochemistry is summarized in Scheme 3. In the early stages of this work we used *rac*-(10) in trimethylsilyl triflate (TMSOTf) promoted glycosidation reactions with the *C*-residue glycosyl trichloroacetimidate (16), thereby providing an easily separable mixture of diastereomeric β-glycosides (17) (30%) and (18) (34%).[27–29] It was much easier to perform the glycosidation reaction using (16) as the resolving agent than to perform the lipase-mediated resolution of (10) on a large scale. We also anticipated that both (17) and (18) could be elaborated to aureolic acid analogues (see below) by using the glycosidation sequence employed in our olivomycin A total synthesis.[20] The stereochemistry at the C2 acyloin centre was determined by glycosidation of enzymatically resolved (*S*)-(10) with (16), which provided (18) in 63% yield. The triethylsilyl (TES) ether of (18) was removed by treatment with HF/pyridine in a tetrahydrofuran (THF)/pyridine solvent mixture, giving alcohol (19) in 88% yield.[30] Glycosidation of (19) with the D–E disaccharide trichloroacetimidate (20)[20] provided, after high-performance liquid chromatography (HPLC) separation, trisaccharide (23) in 38% yield, the chloroacetyl migration product (21) (21%), and diol (22) (9%). Optimal conditions for the glycosidation reaction entailed use of 0.3 equiv. of *tert*-butyldimethylsilyl triflate (TBSOTf) as the promoter at –15°C. Lower reaction temperatures and/or use of TMSOTf resulted in the exclusive formation of (21) and (22). This example adds to the growing list of cases in which TBSOTf has proven superior to TMSOTf for glycosidations of sensitive substrates.[20,31,32]

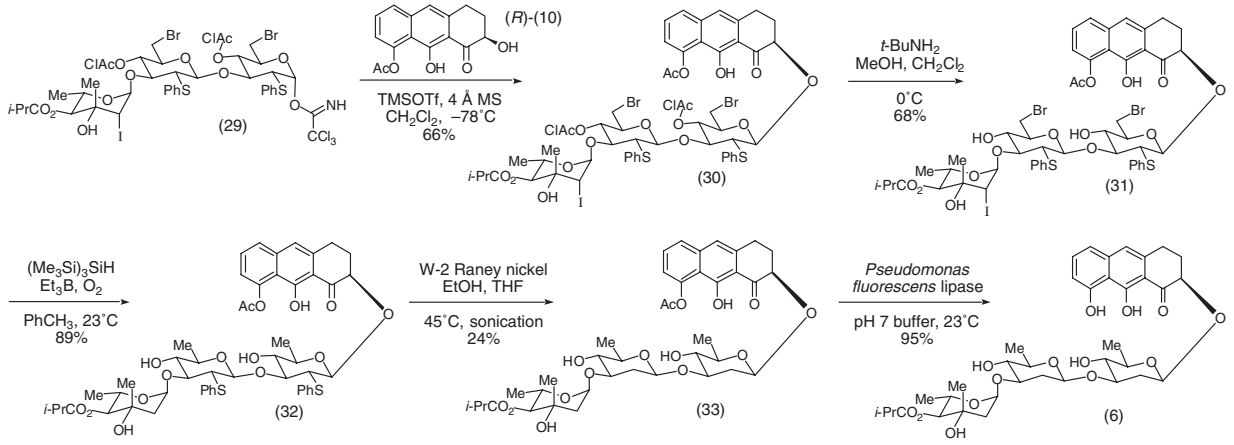
The fully elaborated trisaccharide (23) was readily converted into analogue (5) by a three-step sequence. The chloroacetyl (ClAc) groups were removed selectively by treating (23) with methanolic NH_3 in CH_2Cl_2 at 0°C to provide diol (24). Cleavage of the phenolic acetate group was avoided by stopping the reaction at 50% conversion, HPLC separation of the product, and resubmission of unreacted (23) and the monochloroacetate intermediates to the reaction conditions. This process was repeated three times, giving (24) in 59% yield. The three halogen substituents and two thiophenyl groups were then removed in a single step by using freshly prepared W-2 RaNi[33] in EtOH/THF at 45°C with sonication, giving the penultimate phenolic acetate intermediate (25) in 49% yield. Finally, deprotection of the phenolic acetate was accomplished by using $NaHCO_3$ in aqueous methanol, which provided analogue (5) with natural (2*S*) stereochemistry in 70% yield. Interestingly, epimerization of the C2 acyloin centre was relatively slow under these conditions, in striking contrast to our experience with intermediate (33) in the synthesis of analogue (6) (see below). Use of KCN–MeOH[34] for the final deprotection of (25) resulted in rapid decomposition, while use of NH_3 or *n*-$BuNH_2$/MeOH gave slower rates and correspondingly lower yields than the $NaHCO_3$ protocol.

It was also of interest to synthesize the (2*R*)-analogue (6), in order to determine the role of the stereochemistry of the acyloin C2 stereocentre on DNA binding and Mg^{2+} complex formation. Unfortunately, the 'C + DE' coupling strategy employed for the synthesis of (5) was not successful for the synthesis of (6) (Scheme 4). Deprotection of the TES ether (17) provided alcohol (26) in quantitative yield. However, all attempts to synthesize the protected trisaccharide (30) by coupling of (26) with the D–E disaccharide trichloroacetimidate (20) were unsuccessful. The only products obtained from these experiments were the chloroacetyl migration product (27) and the diol (28).



Scheme 4. Attempted glycosidation of (26).

Accordingly, we synthesized the simplified aureolic acid analogue (6) [with unnatural (2*R*)-stereochemistry] in the manner summarized in Scheme 5. Glycosidation of aglycone (*R*)-(10) using the C–D–E trisaccharide trichloroacetimidate



Scheme 5. Synthesis of aureolic acid analogue (6) with unnatural (2*R*)-acyloin stereochemistry.

(29)* as the glycosyl donor and TMSOTf as the activating agent provided the trisaccharide conjugate (30) in 66% yield.[28] None of the corresponding α-glycoside was detected. The two chloroacetyl protecting groups were removed selectively in the presence of the phenolic acetate, giving diol (31) in 68% yield, by using *t*-$BuNH_2$ in MeOH.† Use of other amines for this deprotection step resulted in competitive cleavage of the C8 phenolic acetate and imine formation (when NH_3 was used). Attempted one-step reduction of the halogen and thiophenyl substituents in (31) using RaNi in a mixture of THF and EtOH gave (33) in very low yield (4%). The poor efficiency of this reaction presumably reflects the lability of the phenolic acetate unit under these conditions, together with strong complexation of the fully-deprotected trisaccharide conjugate (6) with the RaNi catalyst. Better results were obtained when reductive cleavage of the halogen substituents was decoupled from the desulfurization step. Thus, reduction of (31) with tris(trimethylsilyl)silane[35] at ambient temperature using Et_3B and a trace of O_2 as the radical initiator[36] provided (32) in excellent yield (89%). Reduction of a solution of (32) in EtOH/THF with freshly prepared W-2 RaNi[33] in a preheated (45°C) sonication bath then provided (33) in 24% yield (optimized). Deprotection of the remaining C8 phenolic acetate proved somewhat tricky to accomplish without epimerization of the C2 acyloin stereocentre. Use of $NaHCO_3$ in aqueous MeOH, conditions that were successful in the (2*S*)-epimer series (see above), resulted in substantial epimerization of the acyloin C2 centre. Since the C8 acetate had proven labile under the conditions of the enzymatic resolution conditions employed in the synthesis of (*R*)-(10), use of a lipase to hydrolyse the phenolic acetate under very mild conditions was explored. To our considerable delight, treatment of acetate (33) with PFL in pH 7 buffer gave the targeted aureolic acid analogue (2*R*)-(6) in excellent yield with no detectable epimerization of C2.‡

Conclusion

Syntheses of aureolic acid analogues (5) and (6) with (2S)- and (2R)-acyloin stereochemistry, respectively, have been developed. It is clear from the results presented in Schemes 3–5 that the one-step glycosidation sequence leading to trisaccharide conjugate (30) (Scheme 5) is more efficient than the 'C + DE' approach utilized in the synthesis of (23) (Scheme 3). Nevertheless, sufficient quantities of (23), and hence also analogue (5), were prepared by the latter route, so that we did not need to develop a route to (23) involving the glycosidation of (S)-(10) with (20). The considerably different behaviour of the intermediates in the two analogue syntheses is also striking. This is especially evident by comparison of the conditions required for the reductive conversion of (24) into (25) in Scheme 3 versus the conversion of (31) into (33) in Scheme 5, as well as in the considerably greater sensitivity of (33) to base-catalysed epimerization (Scheme 5) compared with (25) (Scheme 3). Finally, the sensitivity of (18) (Scheme 3) and (26) (Scheme 4) towards chloroacetate migration is also noteworthy, especially since comparable problems were not encountered in our olivomycin A synthesis.[20]

The syntheses of (5) and (6) highlight additional limitations in the use of 2-thiophenyl glycosyl donors for synthesis of 2-deoxy-β-glycosides, specifically the difficulty of identifying a protecting group for the C8 phenol that is fully compatible with the conditions required for reductive removal of the thiophenyl substituent after completion of the glycosidation sequence. The 2-deoxy-2-iodoglycosyl donor

*Trisaccharide trichloracetimidate (29) was synthesized by appropriate modifications of our previously published route to the corresponding bis-*C*6-*O*-tosyl C–D–E trisaccharide trichloracetimidate (see supporting information to ref. 27). Complete details will be provided in a full paper detailing our total synthesis of olivomycin A.

†This reagent combination showed the greatest selectivity for hydrolysis of the chloroacetates and minimization of a number of side reactions, and was chosen after screening a number of reagents or other amine bases such as thiourea, NH_3, NH_2NH_2, *n*-$BuNH_2$, and Et_3N. See also A. Lubineau, E. Meyer, P. Place, Carbohydr. Res. **1992**, *228*, 191.

‡For an earlier example of a lipase-mediated hydrolysis of a phenolic acetate, see ref. 24.

glycosidation methodology that we recently introduced promises to solve this problem[32,37] and will be adopted in our future work on the synthesis of DNA-binding aureolic acid analogues.

Studies of the DNA binding properties and Mg^{2+} complex formation of (5) and (6) are in progress and will be reported in due course.

Experimental

General

All reactions were conducted in flame-dried or oven-dried glassware under an atmosphere of dry nitrogen. All solvents were purified before use unless otherwise indicated. THF was distilled from sodium benzophenone ketyl; toluene, Et_3N, and pyridine were distilled from CaH_2; CH_2Cl_2 was distilled from CaH_2 or P_2O_5; MeOH was distilled from Mg turnings. Crushed 4 Å molecular sieves were activated by flame-drying under high vacuum immediately prior to use. Solvents were removed on a rotary evaporator at reduced pressure. Reagents were purchased and used without further purification.

Analytical thin-layer chromatography (TLC) was performed on Kieselgel 60 F_{254} glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized by shortwave and longwave ultraviolet (UV) light and/or ceric ammonium molybdate stain. Flash column chromatography was performed according to the method of Still on Kieselgel 60 (230–400 mesh) silica gel.[38] Preparative normal-phase HPLC purification was performed using an HPLC system composed of two Rainin HPXL pumps and a Rainin Dynamax® UV-C detector connected to either a 10 by 250 mm or a 21 by 250 mm Dynamax® axial compression column packed with Rainin 60 Å irregular silica gel. Preparative reverse-phase HPLC purifications were performed by using a 10 by 250 mm Dynamax® 60A C_{18} polymer-supported column.

Infrared (IR) spectra were recorded as thin films on NaCl plates or as KBr pellets using a Perkin–Elmer Spectrum 1000 FT–IR spectrophotometer. UV spectra were recorded on a Shimadzu PC160+ spectrophotometer using quartz solution cells. Melting points are uncorrected. Optical rotations were measured on a Rudolph Autopol III polarimeter using a quartz cell with 1 mL capacity and a 10 cm path length. ^{1}H NMR spectra were measured at 400 MHz on a Varian Inova 400 instrument or at 500 MHz on a Varian Inova 500 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in δ units using residual chloroform (7.26 ppm) as an internal reference. ^{13}C NMR spectra were measured at 100 or 125 MHz using residual chloroform (77.0 ppm) as an internal reference. High-resolution mass spectra (HRMS) were measured on a VG 70-250-S Micromass spectrometer. Elemental analyses were performed by the University of Michigan CHN Laboratory.

*8-Acetoxy-9-hydroxy-3,4-dihydro-1(2*H*)-anthracenone (9)*

A flame-dried 100 mL round-bottom flask was charged with diphenol ketone (8) (913 mg, 4.00 mmol),[15,16] CH_2Cl_2 (32 mL) and pyridine (8 mL), and cooled in an ice bath. Acetyl chloride (0.37 mL, 5.2 mmol, 1.3 equiv.) was added dropwise. After the addition was complete, the ice bath was removed, and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into a separatory funnel containing saturated aqueous $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (× 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum, followed by co-evaporation from heptane to remove residual pyridine. Purification of the crude product by flash chromatography (SiO_2; 15% EtOAc/hexanes–2% MeOH, then 20% EtOAc/hexanes–2% MeOH) gave (9) (978 mg, 90%) as an orange *solid*, m.p. 136–138°C (Found: C, 70.5; H, 5.6%; M^+ (EI), 270.0892. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.7%; M^+, 270.0892). FT–IR (KBr) 3447, 3026, 2948, 2875, 1764, 1618, 1459, 1399, 1377, 1356, 1310, 1198, 1167, 1042, 884, 841, 782 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.08, quintet, *J* 6.4 Hz, 2H; 2.41, s, 3H; 2.73, dd, *J* 6.4, 6.4 Hz, 2H; 2.96, dd, *J* 6.2, 6.2 Hz, 2H; 7.01, m, 2H; 7.52, m, 2H; 14.80, s, 1H. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 22.6, 30.0, 38.9, 112.2, 116.7, 117.2, 118.9, 125.4, 130.2, 139.0, 139.5, 148.9, 163.3, 170.3, 205.2.

*8-Acetoxy-2,9-dihydroxy-3,4-dihydro-1(2*H*)-anthracenone,* rac*-(10)*

A 250 mL round-bottom flask, flame-dried under N_2, was charged with ketone (9) (950 mg, 3.51 mmol) and CH_2Cl_2 (35 mL). The dark yellow solution was cooled to –78°C and Et_3N (4.0 mL, 28.1 mmol, 8 equiv.) was added, followed by the dropwise addition of TMSOTf (2.54 mL, 14.1 mmol, 4 equiv.). The resulting fluorescent-yellow suspension was stirred at –78°C for 1 h, and then poured into 150 mL of saturated aqueous $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (× 2). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was dissolved in dry CH_2Cl_2 (25 mL), flushed with N_2, and the solution was cooled to –78°C. Solid $NaHCO_3$ (591 mg, 7.02 mmol, 2 equiv.) was added, followed by recrystallized *m*-CPBA (1.21 g, 7.02 mmol, 2 equiv.). The resulting slurry was stirred vigorously while warming to 0°C over 3–4 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (50 mL), and then saturated aqueous $NaHSO_3$ (50 mL) was added carefully to avoid foaming. The biphasic mixture was stirred vigorously for 30 min and then poured into a separatory funnel containing saturated aqueous $NaHCO_3$ (100 mL) and saturated aqueous Na_2HSO_3 (100 mL). The aqueous layer was extracted with CH_2Cl_2 (× 4). The organic layers were dried over Na_2SO_4 and concentrated. The residue was dissolved in MeOH (20 mL) and transferred to a 100 mL flask. The flask was flushed with N_2, and the solution was heated to reflux overnight. The solution was concentrated, and then the crude product was purified by flash chromatography (SiO_2; 20% EtOAc/hexanes–2% MeOH, then 30% EtOAc/hexanes–2% MeOH) to give *rac*-(10) (813 mg, 81%) as a yellow *solid*, m.p. 126–131°C (Found: C, 66.6; H, 5.1%; $[M + H]^+$ (CI/NH_3), 287.0912. $C_{16}H_{14}O_5$ requires C, 67.1; H, 4.9%; $[M + H]^+$, 287.0919). FT–IR (KBr) 3467, 3060, 3026, 2942, 2875, 2836, 1764, 1629, 1573, 1493, 1459, 1437, 1399, 1375, 1322, 1206, 1174, 1074, 1040, 994, 950, 916, 888, 849, 772 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.05, ddd, *J* 12.5, 12.1, 5.9 Hz, 1H; 2.41, s, 3H; 2.51, m, 1H; 3.09, m, 2H; 3.77, s, 1H; 4.41, dd, *J* 12.8, 5.5 Hz, 1H; 7.05, dd, *J* 6.8, 1.6 Hz, 1H; 7.09, s, 1H; 7.55, m, 2H; 13.85, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 27.5, 30.8, 73.2, 110.4, 117.0, 117.5, 119.4, 125.6, 130.7, 138.4, 139.9, 148.9, 163.2, 170.3, 204.3.

Enzymatic Resolution of rac*-(10) with* Pseudomonas fluorescens *Lipase*

A flame-dried 100 mL round-bottom flask was charged with racemic α-hydroxy ketone (10) (427 mg, 1.49 mmol) and vinyl acetate (40 mL) freshly distilled from glass. *Pseudomonas fluorescens* lipase (380 mg, Fluka) was added, and the cloudy suspension was stirred vigorously at room temperature. ^{1}H NMR analysis of an aliquot after 5 h showed 50% conversion. The suspension was filtered through a Celite plug, the plug rinsed with CH_2Cl_2, and the filtrate was concentrated under vacuum. Purification of the crude product by flash chromatography (SiO_2; 25% EtOAc/hexanes–2% MeOH, then 30% EtOAc/hexanes–2% MeOH) gave acetate (*R*)-(11) (235 mg, 48%) and alcohol (*S*)-(10) (200 mg, 47%), $[\alpha]_D^{25}$ –44.9° (*c*, 1.05 in $CHCl_3$).

*(2*R*)-2,8-Diacetoxy-9-hydroxy-3,4-dihydro-1(2*H*)-anthracenone (11)*, m.p. 145–147°C (Found: C, 65.5; H, 5.0%; M^+ (EI), 328.0938. $C_{18}H_{16}O_6$ requires C, 65.9; H, 4.9%; M^+, 328.0947). $[\alpha]_D^{25}$ +154.1° (*c*, 1.19 in $CHCl_3$). FT–IR (KBr) 3435, 3090, 2949, 2889, 2852, 1758, 1630, 1602, 1572, 1495, 1459, 1437, 1373, 1340, 1303, 1230, 1203, 1178, 1100, 1040, 989, 893, 849, 765, 709, 684 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.24, s, 3H; 2.27, m, 1H; 2.37, m, 1H; 2.38, s, 3H; 3.16, m, 1H; 5.64, dd, *J* 12.6, 5.3 Hz, 1H; 7.05, dd, *J* 6.6, 1.8 Hz, 1H; 7.09, s, 1H; 7.55, m, 2H; 14.19, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.8, 21.2, 27.7, 28.6, 73.3, 111.2, 117.1, 117.2, 119.5, 125.6, 130.8, 137.4, 139.7, 149.0, 163.8, 170.2, 170.3, 199.1.

*(2*R*)-8-Acetoxy-2,9-dihydroxy-3,4-dihydro-1(2*H*)-anthracenone* (R)-*(10)*

Pseudomonas fluorescens lipase (47 mg, Fluka) was dissolved in phosphate buffer (25 mL, pH 7, 50 mM). A solution of diacetate (*R*)-(11) (53.0 mg, 0.161 mmol) in CH_2Cl_2 (4 mL) was added to the buffer–lipase solution. The biphasic mixture was stirred vigorously at room temperature for 19 h, CH_2Cl_2 (20 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (× 3). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and co-evaporated twice from toluene. The brownish-yellow solid was dissolved in CH_2Cl_2 (5 mL) and pyridine (2 mL), and cooled to –15°C in an acetone/ice bath. Ac_2O (16 μL, 0.165 mmol, 1.1 equiv.) was added dropwise and the solution was allowed to warm gradually to 0°C over 7 h. The solution was poured into 1 M $KHSO_4$ (50 mL) and shaken vigorously. The aqueous layer was extracted with CH_2Cl_2 (× 3) and the combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuum. Purification of the crude product by flash chromatography (SiO_2; 25% EtOAc/hexanes–2% MeOH) gave (*R*)-(10) (32.4 mg, 70%) as a yellow solid, $[\alpha]_D^{25}$ +48.9° (*c*, 0.72 in $CHCl_3$).

Coupling of (S)*-(10) and Trichloroacetimidate (16): Synthesis of* β*-Glycoside (18)*

A flame-dried 10 mL round-bottom flask was charged with α-hydroxy ketone (*S*)-(10) (50.0 mg, 0.175 mmol, 1 equiv.), 4 Å molecular sieves (44 mg) flame-dried under vacuum, and CH_2Cl_2 (2.2 mL) distilled from P_2O_5. Trichloroacetimidate (16)[20] 164 mg, 0.227 mmol, 1.3 equiv.) was added, and the cloudy yellow suspension was stirred at ambient temperature for 20 min. The solution was cooled to –78°C in a dry ice/acetone bath, then TMSOTf (10 μL, 0.052 mmol, 0.3 equiv.) was added in a single portion. The suspension was stirred at –78°C for 45 min, and then the reaction was quenched by addition of Et_3N (0.2 mL). The mixture was filtered through a Celite plug, and the filtrate was washed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (× 3). The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the crude product by flash chromatography (SiO_2; 15% EtOAc/hexanes, then 15% EtOAc/hexanes–2% MeOH), followed by preparative HPLC (25% EtOAc/hexanes, 21 mm column, 10 mL min^{-1}, λ 290 nm, t_R 16.4 min) gave the β-glycoside (18) (86.7 mg, 63%) as a yellow glassy *foam* (Found (FAB): $[M + Na]^+$, 815.0994. $C_{36}H_{42}BrClO_9SSi$ requires $[M + Na]^+$, 815.1088). $[\alpha]_D^{25}$ +107.1° (*c*, 1.01 in $CHCl_3$). FT–IR (thin film) 3520, 3059, 2956, 2913, 2877, 1766, 1630, 1575, 1461, 1440, 1401, 1380, 1335, 1307, 1238, 1207, 1173, 1161, 1134, 1109, 1065, 1046, 1014, 912, 884, 854, 823, 802, 739, 689 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.64, m, 6H; 0.92, t, *J* 7.9 Hz, 9H; 2.11, m, 2H; 2.43, s, 3H; 2.71, dd, *J* 6.0, 6.0 Hz, 2H; 3.21, dd, *J* 10.3, 8.6 Hz, 1H; 3.41, dd, *J* 11.0, 7.9 Hz, 1H; 3.46, dd, *J* 11.0, 3.3 Hz, 1H; 3.68, ddd, *J* 9.5, 7.7, 3.3 Hz, 1H; 3.77, dd, *J* 9.9, 8.1 Hz, 1H; 4.13, s, 2H; 4.46, dd, *J* 6.6, 4.0 Hz, 1H; 4.97, dd, *J* 9.2, 8.2 Hz, 1H; 5.05, d, *J* 8.8 Hz, 1H; 6.91, m, 4H; 7.05, dd, *J* 7.3, 1.5 Hz, 1H; 7.16, m, 2H; 7.52, dd, *J* 8.4, 1.3 Hz, 1H; 7.57, t, *J* 7.7 Hz, 1H; 14.39, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 5.4 (3C), 6.8 (3C), 21.2, 25.2, 29.3, 31.2, 40.8, 56.6, 72.6, 73.1, 75.7, 76.6, 102.7, 111.1, 116.9, 117.1, 119.2, 125.5, 126.3, 128.3 (2C), 130.6, 130.7 (2C), 138.4, 139.7, 149.0, 164.2, 166.4, 170.3, 200.6.

Use of racemic (10) in this glycosidation reaction provided (17) and (18) in 30 and 34% yields, respectively. Data for (17): (Found (FAB): $[M + Na]^+$, 815.1066. Calc. for $C_{36}H_{42}BrClO_9SSi$: $[M + Na]^+$, 815.1088). HPLC (25% EtOAc/hexanes, 21 mm column, 10 mL min^{-1}, t_R 19.9 min). $[\alpha]_D^{25}$ –55.7° (*c*, 1.09 in $CHCl_3$). FT–IR (thin film) 3475, 3351, 3295, 3060, 2956, 2876, 1763, 1631, 1604, 1575, 1461, 1440, 1401, 1380, 1333, 1302, 1239, 1207, 1173, 1160, 1135, 1108, 1066, 1046, 1015, 913, 885, 850, 823, 802, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.65, m, 6H; 0.93, t, *J* 7.9 Hz, 9H; 1.96, m, 1H; 2.14, m, 1H; 2.39, s, 3H; 2.79, ddd, *J* 16.7, 7.3, 4.2 Hz, 1H; 3.05, ddd, *J* 16.7, 8.1, 4.0 Hz, 1H; 3.31, dd, *J* 9.9, 8.4 Hz, 1H; 3.36, dd, *J* 5.5, 1.5 Hz, 1H; 3.65, m, 1H; 3.78, dd, *J* 10.1, 8.2 Hz, 1H; 4.12, s, 2H; 4.40, dd, *J* 7.7, 3.7 Hz, 1H; 4.78, d, *J* 8.4 Hz, 1H; 4.96, dd, *J* 8.4, 9.5 Hz, 1H; 6.99, s, 1H; 7.01, dd, *J* 7.0, 1.5 Hz, 1H; 7.14, tt, *J* 7.3, 1.1 Hz, 1H; 7.20, t, *J* 7.3 Hz, 2H; 7.42, d, *J* 7.3 Hz, 2H; 7.49, dd, *J* 8.1, 1.5 Hz, 1H; 7.53, t, *J* 7.5 Hz, 1H; 14.31, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz,) δ 5.4 (3C), 6.9 (3C), 21.2, 25.6, 28.0, 30.8, 40.8, 56.7, 72.9, 73.6, 75.5, 76.5, 102.2, 111.3, 116.9, 117.1, 119.2, 125.5, 126.6, 128.7 (2C), 130.3 (2C), 130.5, 135.2, 137.8, 139.6, 149.0, 164.0, 166.3, 170.3, 199.9.

Deprotection of (18): Synthesis of Monosaccharide Alcohol (19)

A solution of triethylsilyl ether (18) (272 mg, 0.343 mmol) in THF (10 mL) was flushed with N_2 and cooled in an ice bath. Pyridine (1 mL) was added, followed by the dropwise addition of HF/pyridine complex (1 mL). The reaction mixture was stirred at 0°C for 45 min. The mixture was carefully diluted with saturated aqueous $NaHCO_3$, then was poured into a separatory funnel containing saturated aqueous $NaHCO_3$ and extracted with EtOAc (× 3). The combined organics were washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, concentrated under vacuum, and co-evaporated from heptane to remove residual pyridine. Purification of the crude product by flash chromatography (SiO_2; 30% EtOAc/hexanes, then 40% EtOAc/hexanes) gave (19) (205 mg, 88%) as a yellow *oil* (Found (FAB): $[M + Na]^+$, 701.0202. $C_{30}H_{28}BrClO_9S$ requires $[M + Na]^+$, 701.0224). $[\alpha]_D^{26}$ +59.5° (*c*, 0.68 in $CHCl_3$). FT–IR (thin film) 3503, 3058, 2953, 2876, 1760, 1630, 1574, 1458, 1440, 1378, 1334, 1307, 1207, 1173, 1161, 1107, 1046, 1011, 912, 886, 853, 733 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.26, m, 1H; 2.32, m, 1H; 2.44, s, 3H; 2.88, ddd, *J* 16.5, 7.7, 4.6 Hz, 2H; 3.01, m, 2H; 3.07, dd, *J* 10.6, 8.8 Hz, 1H; 3.43, dd, *J* 11.4, 7.7 Hz, 1H; 3.51, dd, *J* 11.0, 2.7 Hz, 1H; 3.59, dd, *J* 10.6, 9.0 Hz, 1H; 3.66, ddd, *J* 7.7, 7.7, 2.6 Hz, 1H; 4.14, s, 2H; 4.56, dd, *J* 8.1, 4.2 Hz, 1H; 4.94, d, *J* 8.8 Hz, 1H; 5.02, dd, *J* 9.3, 9.3 Hz, 1H; 7.05, s, 1H; 7.08, dd, *J* 7.0, 1.5 Hz, 1H; 7.12, t, *J* 7.3 Hz, 2H; 7.17, d, *J* 7.3 Hz, 2H; 7.40, dd, *J* 8.7, 1.6 Hz, 2H; 7.57, m, 2H; 14.45, s, 1H. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 25.8, 29.7, 30.9, 40.6, 56.7, 60.3, 71.1, 72.7, 75.2, 76.4, 101.4, 111.2, 117.0, 119.3, 125.5, 128.0, 128.8 (2C), 130.7, 133.5 (2C), 138.2, 139.7, 148.9, 164.2, 166.5, 170.3, 200.8.

*Fully Protected Trisaccharide, (2*S*)-Epimer (23)*

A mixture of alcohol (19) (198 mg, 0.291 mmol, 1 equiv.), D–E disaccharide trichloroacetimidate (20)[20] (381 mg, 0.426 mmol, 1.5 equiv.), 4 Å molecular sieves (100 mg) activated under vacuum, and CH_2Cl_2 (4 mL) distilled from P_2O_5 was stirred at ambient temperature for 30 min and then cooled to –15°C in an ice/acetone bath. TBSOTf (20 μL, 0.087 mmol, 0.3 equiv.) was added in one portion, and the reaction mixture was allowed to warm gradually to 0°C with stirring over 2 h. An additional 10 μL of TBSOTf was added, and the mixture was stirred at 0°C for another 1.5 h. The reaction was quenched by addition of Et_3N (0.5 mL) and the mixture was filtered through a Celite plug and rinsed with CH_2Cl_2. The filtrate was washed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (× 2). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash chromatography (SiO_2; 25% EtOAc/hexanes, then 40% EtOAc/hexanes) followed by preparative HPLC (40% EtOAc/hexanes, 21 mm column, 10 mL min^{-1}, λ 290 nm) gave (23) (155 mg, 38%) as a yellow glass that contained inseparable impurities. This material was used directly in the following step without additional purification. In addition, the acyl transfer product (21) (41 mg, 21%) and diol (22) (15 mg, 9%) were also isolated. Partial data for impure (23): ^1H NMR ($CDCl_3$, 500 MHz) δ 1.14, d, *J* 6.2 Hz, 3H; 1.16, d, *J* 7.0 Hz, 6H; 1.19, s, 3H; 2.06, m, 1H; 2.14, m, 1H; 2.25, s, 1H; 2.44, s, 3H; 2.57, septet, *J* 7.0 Hz, 1H; 2.68, m, 2H; 3.17, dd, *J* 9.8, 9.8 Hz, 1H; 3.24, dd, *J* 9.3, 9.3 Hz, 1H; 3.36, dd, *J* 11.5, 7.9 Hz, 1H; 3.43, dd, *J* 11.4, 7.0 Hz, 1H; 3.62–3.50, m, 5H; 3.78, m, 2H; 4.11, ABq, J_{AB} 15.0 Hz, 1H; 4.15, ABq, J_{AB} 15.0 Hz, 1H; 4.21, ABq, J_{AB} 15.0 Hz, 1H; 4.27, ABq, J_{AB} 15.0 Hz, 1H; 4.44, dd, *J* 6.4, 3.8 Hz, 1H; 4.51, s, 1H; 4.88, d, *J* 8.8 Hz, 1H; 4.91, dd, *J* 9.2, 9.2 Hz, 1H; 5.01, dd, *J* 9.2, 9.2 Hz, 1H; 5.04, d, *J* 8.4 Hz, 1H; 5.16, d, *J* 9.2 Hz, 1H; 5.39, s, 1H; 6.87, t, *J* 7.5 Hz, 2H; 6.93, s, 1H; 6.98, t, *J* 7.3 Hz, 1H; 7.07, d, *J* 7.3 Hz, 1H; 7.13, d, *J* 7.3 Hz, 2H; 7.18, t, *J* 7.3 Hz, 1H; 7.30, d, *J* 7.7 Hz, 2H; 7.37, d, *J* 7.7 H_2, 2H; 7.53, d, *J* 8.1 Hz, 1H; 7.59, t, *J* 7.8 Hz, 1H; 14.39, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ

17.4, 18.8, 18.9 (2C), 20.6, 21.3, 25.1, 29.3, 30.8, 31.0, 34.1 (2C), 40.9, 41.1, 46.1, 54.1, 54.9, 68.6, 70.8, 72.2, 72.5, 73.3, 74.7, 75.6, 76.1, 76.9, 82.1, 102.1, 103.1, 105.2, 111.1, 117.0, 119.2, 125.5, 126.2, 126.9, 128.4 (2C), 128.5 (2C), 129.0 (2C), 130.7, 131.6 (2C), 133.4, 135.2, 138.3, 139.8, 149.0, 164.3, 166.3, 166.4, 170.3, 177.1, 200.5.

Deprotection of Trisaccharide (23): Synthesis of Trisaccharide Triol (24)

A solution of slightly impure trisaccharide (23) (142 mg, 0.114 mmol) in CH_2Cl_2 (6 mL) was cooled in an ice bath. A methanolic NH_3 solution (6 mL, 2 M) was added slowly. The reaction mixture was stirred until homogeneous, and then was allowed to stand without stirring at 0°C for 4 h until the reaction was about 50% complete by TLC analysis. The light-red solution was poured into 1 M $KHSO_4$ (75 mL) and extracted with CH_2Cl_2 (× 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by preparative HPLC (40% EtOAc/hexanes, 21 mm column, 10 mL min^{-1}, λ 290 nm, t_R 16.35 min) gave diol (24) (47.8 mg, 38%) and a mixture of (23) and monochloroacetates (68.7 mg). The latter mixture was resubmitted to the reaction conditions to give a combined yield of triol (24) (74.7 mg, 59%) as a yellow *glass* (Found (FAB): $[M + Na]^+$, 1283.0. $C_{51}H_{57}Br_2IO_{15}S_2$ requires $[M + Na]^+$, 1283.8). $[\alpha]_D^{25}$ +111.1° (*c*, 0.46 in $CHCl_3$). FT–IR (thin film) 3488, 3058, 2976, 2938, 2877, 1739, 1626, 1576, 1472, 1457, 1439, 1400, 1380, 1359, 1335, 1258, 1205, 1173, 1160, 1085, 1044, 912, 884, 853, 814, 735 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.18, d, *J* 7.0 Hz, 3H; 1.19, d, *J* 7.0 Hz, 3H; 1.30, s, 3H; 1.31, d, *J* 5.1 Hz, 3H; 2.13, m, 3H; 2.22, s, 1H; 2.42, s, 3H; 2.60, septet, *J* 7.0 Hz, 1H; 2.70, m, 2H; 3.15, dd, *J* 10.6, 9.2 Hz, 1H; 3.20, dd, *J* 10.6, 8.8 Hz, 1H; 3.38, dd, *J* 11.0, 7.7 Hz, 1H; 3.49, m, 4H; 3.58, ddd, *J* 10.8, 7.6, 7.6 Hz, 2H; 3.65, dd, *J* 11.4, 4.8 Hz, 1H; 3.77, dd, *J* 11.2, 2.4 Hz, 1H; 3.83, dd, *J* 12.3, 1.8 Hz, 1H; 3.85, s, 1H; 4.04, s, 1H; 4.07, dd, *J* 6.8, 6.8 Hz, 1H; 4.27, d, *J* 3.3 Hz, 1H; 4.46, dd, *J* 6.3, 4.0 Hz, 1H; 4.92, d, *J* 8.8 Hz, 1H; 4.95, d, *J* 7.3 Hz, 1H; 4.99, d, *J* 8.8 Hz, 1H; 5.35, d, *J* 3.7 Hz, 1H; 6.77, t, *J* 7.7 Hz, 2H; 6.87, t, *J* 7.5 Hz, 1H; 6.92, s, 1H; 7.05, dd, *J* 7.3, 1.1 Hz, 1H; 7.11, dd, *J* 7.7, 1.5 Hz, 2H; 7.18, d, *J* 7.0 Hz, 1H; 7.22, t, *J* 7.3 Hz, 2H; 7.32, dd, *J* 7.3, 1.5 Hz, 2H; 7.51, dd, *J* 8.4, 1.1 Hz, 1H; 7.56, t, *J* 7.7 Hz, 1H; 14.40, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.4, 18.8, 18.9, 21.3, 23.0, 29.4, 32.1, 32.8, 34.0 (2C), 43.9, 54.3, 54.6, 70.1, 71.6, 71.7, 72.2, 73.7, 74.5, 75.1, 75.8, 82.0, 85.4, 102.8, 102.9, 103.5, 111.1, 116.9, 117.1, 119.2, 125.5, 126.4, 126.6, 128.1 (2C), 128.9 (2C), 130.1 (2C), 130.6, 131.2 (2C), 134.3, 135.3, 138.4, 139.7, 149.0, 164.2, 170.3, 176.6, 200.6.

RaNi Reduction of (24): Synthesis of Phenolic Acetate (25)

A flame-dried 25 mL round-bottom flask was charged with (24) (52.8 mg, 0.0419 mmol), dry THF (8 mL), and 120 pipette drops of freshly prepared W-2 Raney nickel suspension in EtOH.[33] The suspension was sonicated for 3 h, while the bath temperature was kept below 45°C. An additional 90 drops of RaNi suspension were added every 60 min, until TLC analysis showed 100% conversion of (24). The greenish-black suspension was diluted with MeOH and filtered through a Celite plug to remove the nickel metal. The filter pad was rinsed with MeOH and the combined filtrate was concentrated. The residue was passed through a SiO_2 plug, with 75% EtOAc/hexanes–2% MeOH as eluent, and was then purified by preparative HPLC (80% EtOAc/hexanes, 21 mm column, 10 mL min^{-1}, λ 290 nm, t_R 17.2 min) to give (25) (15.6 mg, 49%) as a yellow *glass* (Found (FAB): $[M + Na]^+$, 783.3279. $C_{39}H_{52}O_{15}$ requires $[M + Na]^+$, 783.3204). $[\alpha]_D^{25}$ –118.6° (*c*, 0.36 in $CHCl_3$). FT–IR (thin film) 3430, 2975, 2936, 2879, 1765, 1735, 1630, 1576, 1457, 1367, 1333, 1204, 1162, 1127, 1069, 1022, 907, 852, 755 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.21, d, *J* 7.0 Hz, 3H; 1.22, d, *J* 7.0 Hz, 3H; 1.23, d, *J* 7.3 Hz, 3H; 1.35, s, 3H; 1.38, d, *J* 6.2 Hz, 3H; 1.39, d, *J* 6.2 Hz, 3H; 1.68, ddd, *J* 12.1, 12.1, 10.3 Hz, 1H; 1.72, ddd, *J* 12.1, 12.1, 9.9 Hz, 1H; 2.00, dd, *J* 13.9, 4.4 Hz, 1H; 2.04, s, 1H; 2.06, dd, *J* 13.9, 1.8 Hz, 1H; 2.27–2.00, m, 2H; 2.42–2.34, m, 2H; 2.39, s, 3H; 2.64, septet, *J* 7.0 Hz, 1H; 3.16–3.03, m, 3H; 3.18, ddd, *J* 16.5, 4.6, 4.6 Hz, 1H; 3.28, dq, *J* 9.2, 6.2 Hz, 1H; 3.37, dq, *J* 9.2, 6.2 Hz, 1H; 3.48, ddd, *J* 11.9, 8.4, 5.3 Hz, 1H; 3.55, ddd, *J* 11.9, 8.4, 5.3 Hz, 1H; 3.99, dq, *J* 9.5, 6.2 Hz, 1H; 4.07, s, 1H; 4.45, br s, 1H; 4.55, d, *J* 10.6 Hz, 1H; 4.57, dd, *J* 10.6, 3.3 Hz, 1H; 4.59, d, *J* 9.5 Hz, 1H; 4.94, dd, *J* 9.9, 1.8 Hz, 1H; 5.01, dd, *J* 4.2, 2.0 Hz, 1H; 7.04, dd, *J* 6.6, 2.2 Hz, 1H; 7.08, s, 1H; 7.54, m, 2H; 14.37, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.7, 17.8, 17.9, 18.9, 19.0, 21.2, 22.9, 27.2, 30.1, 34.2, 37.1, 37.3, 43.8, 66.6, 70.6, 72.1, 72.2, 75.0, 75.2, 79.4, 80.9, 82.3, 97.3, 99.5, 99.6, 111.3, 117.1 (2C), 119.3, 125.6, 103.6, 138.1, 139.8, 148.9, 163.8, 170.3, 177.5, 203.1.

*Aureolic Acid Analogue (5), (2*S*)-Epimer*

A solution of phenolic acetate (25) (2.1 mg, 0.0027 mmol) in MeOH (0.5 mL) was prepared in a 1 dram screw-capped vial. A solution of saturated $NaHCO_3$ (0.1 mL) in deionized H_2O (0.4 mL) was added dropwise with stirring. The vial was flushed with N_2 and stirred at ambient temperature for 2 h. The solution was poured into a separatory funnel containing H_2O (10 mL), and extracted with CH_2Cl_2 (× 3). The combined organic phases were dried over Na_2SO_4 and concentrated. Purification of the crude product by preparative HPLC (80% EtOAc/hexanes, 10 mm column, 5 mL min^{-1}, λ 265 nm, t_R 7.5 min) gave (5) (1.4 mg, 71%) as a yellow *glass* (Found (FAB): $[M + Na]^+$, 741.3125. $C_{37}H_{50}O_{14}$ requires $[M + Na]^+$, 741.3098). $[\alpha]_D^{25}$ –165.5° (*c*, 0.20 in $CHCl_3$). FT–IR (thin film) 3402, 2975, 2935, 2876, 1734, 1635, 1577, 1450, 1419, 1386, 1345, 1306, 1248, 1161, 1127, 1069, 1022, 907, 852 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.21, d, *J* 6.8 Hz, 3H; 1.22, d, *J* 7.1 Hz, 3H; 1.23, d, *J* 6.4 Hz, 3H; 1.35, s, 3H; 1.38, d, *J* 6.1 Hz, 3H; 2.00, dd, *J* 14.0, 4.3 Hz, 1H; 1.39, d, *J* 6.1 Hz, 3H; 1.69, ddd, *J* 12.3, 12.3, 10.0 Hz, 1H; 1.73, ddd, *J* 12.3, 12.3, 9.9 Hz, 1H; 2.05, dd, *J* 13.9, 2.0 Hz, 1H; 2.22, m, 1H; 2.26, ddd, *J* 12.9, 5.1, 2.0 Hz, 1H; 2.36, ddd, *J* 12.7, 5.4, 2.0 Hz, 1H; 2.39, s, 1H; 2.41, dq, *J* 13.2, 4.8 Hz, 1H; 2.64, septet, *J* 7.1 Hz, 1H; 3.03, ddd, *J* 15.6, 11.0, 3.8 Hz, 1H; 3.16–3.03, m, 3H; 3.30, dq, *J* 9.0, 6.1 Hz, 1H; 3.37, dq, *J* 9.0, 6.2 Hz, 1H; 3.48, ddd, *J* 11.7, 8.3, 5.3 Hz, 1H; 3.57, ddd, *J* 11.7, 8.3, 5.3 Hz, 1H; 3.99, dq, *J* 9.5, 6.2 Hz, 1H; 4.06, s, 1H; 4.48, br s, 1H; 4.56, dd, *J* 10.0, 2.0 Hz, 1H; 4.59, dd, *J* 11.1, 4.5 Hz, 1H; 4.60, d, *J* 9.3 Hz, 1H; 4.96, dd, *J* 9.9, 1.8 Hz, 1H; 5.01, dd, *J* 4.2, 2.0 Hz, 1H; 6.85, d, *J* 7.8 Hz, 1H; 7.00, s, 1H; 7.13, d, *J* 8.1 Hz, 1H; 7.49, t, *J* 7.9 Hz, 1H; 9.60, s, 1H; 15.57, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.8, 17.9, 18.0, 18.9, 19.0, 22.9, 27.2, 30.4, 34.2, 37.1, 37.4, 43.9, 66.6, 70.6, 72.1, 72.2, 75.0, 75.3, 76.6, 79.5, 80.9, 82.2, 97.3, 99.6, 99.8, 109.5, 110.9, 112.5, 117.4, 118.2, 132.9, 136.9, 139.5, 157.9, 165.8, 177.5, 202.9.

Glycosidation of (R)-*(10) with C–D–E Trisaccharide Trichloroacetimidate (29): Synthesis of Trisaccharide (30)*

A flame-dried 10 mL round-bottom flask was charged with acyloin (*R*)-(10) (20.0 mg, 0.067 mmol, 1.5 equiv.) [pre-dried by co-evaporation from PhH (× 2)] and flushed with N_2. Trisaccharide trichloroacetimidate (29)* (65.6 mg, 0.051 mmol, 1 equiv.), 4 Å molecular sieves (30 mg), and CH_2Cl_2 (1.3 mL) (distilled from P_2O_5) were added, and the resulting yellow suspension was stirred at ambient temperature for 15 min. The mixture was cooled to –78°C in a dry ice/acetone bath, and then TMSOTf (4 μL, 0.022 mmol, 0.4 equiv.) was added in a single portion. The reaction mixture was stirred at –78°C for 45 min, quenched with Et_3N, and filtered through a Celite plug which was washed with CH_2Cl_2. The filtrate was extracted with saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with CH_2Cl_2 (× 2). The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the crude product by flash chromatography (SiO2, 30% EtOAc/hexanes–2% MeOH) and then preparative HPLC (40% EtOAc/hexanes, 21 mm column, 10 mL min^{-1}, λ 290 nm, t_R 17.1 min) gave trisaccharide (30) (47.7 mg, 66%) as a yellow *glass* (Found (FAB): [M + Na]+, 1437.0. $C_{55}H_{59}Br_2Cl_2IO_{17}S_2$ requires $[M + Na]^+$, 1437.1). $[\alpha]_D^{25}$ –71.5° (*c*, 0.41 in $CHCl_3$). FT–IR (thin film) 3468, 3453, 3060, 3020, 2974, 2944, 2878, 1763, 1733, 1629, 1604, 1576, 1458, 1439, 1400, 1358, 1334, 1315, 1259, 1204, 1161, 1127, 1046, 1024, 824, 745 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.14, d, *J* 7.0 Hz, 3H; 1.15, d, *J* 7.0 Hz, 3H; 1.16, d, *J* 7.0 Hz, 3H; 1.19,

*See footnote * on p. 116.

s, 3H; 1.89, m, 1H; 2.13, m, 1H; 2.24, s, 1H; 2.39, s, 3H; 2.56, septet, *J* 7.0 Hz, 1H; 2.78, ddd, *J* 16.7, 7.9, 4.2 Hz, 1H; 3.00, ddd, J 16.5, 7.9, 4.0 Hz, 1H; 3.14, dd, *J* 10.8, 9.0 Hz, 1H; 3.34, dd, *J* 7.3, 2.9 Hz, 1H; 3.36, dd, *J* 8.1, 3.5 Hz, 1H; 3.41, dd, *J* 11.0, 2.9 Hz, 1H; 3.48, dd, *J* 11.4, 2.6 Hz, 1H; 3.55, ddd, *J* 7.7, 7.7, 2.6 Hz, 1H; 3.57, dd, *J* 11.0, 8.8 Hz, 1H; 3.74, ddd, *J* 7.3, 7.3, 2.9 Hz, 1H; 3.79, dq, *J* 9.2, 6.2 Hz, 1H; 3.93, dd, *J* 9.0, 9.0 Hz, 1H; 4.10, ABq, J_{AB} 15.0 Hz, 1H; 4.15, ABq, J_{AB} 14.7 Hz, 1H; 4.18, ABq, J_{AB} 14.7 Hz, 1H; 4.23, AB, J_{AB} 15.0 Hz, 1H; 4.37, dd, *J* 8.1, 4.0 Hz, 1H; 4.51, d, *J* 1.8 Hz, 1H; 4.77, d, *J* 8.1 Hz, 1H; 4.88, d, *J* 9.2 Hz, 1H; 4.89, dd, *J* 9.7, 8.6 Hz, 1H; 5.01, dd, *J* 9.7, 8.2 Hz, 1H; 5.04, d, *J* 8.8 Hz, 1H; 5.40, d, *J* 1.5 Hz, 1H; 6.99, s, 1H; 7.02, dd, *J* 7.1, 1.3 Hz, 1H; 7.09, tt, *J* 7.1, 1.1 Hz, 1H; 7.19, m, 5H; 7.25, m, 2H; 7.42, m, 2H; 7.50, dd, *J* 8.4, 1.3 Hz, 1H; 7.54, t, *J* 7.7 Hz, 1H; 14.28, s, 1H. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4, 18.8, 18.9, 20.7, 21.2, 25.7, 28.1, 30.7, 30.8, 34.1, 40.8, 41.0, 46.0, 54.3, 54.9, 60.4, 68.6, 70.8, 72.7, 72.8, 73.3, 74.8, 76.2, 77.3, 78.4, 82.0, 101.5, 103.1, 105.2, 111.3, 116.9, 117.1, 119.2, 125.5, 126.4, 127.4, 128.6, 128.9 (2C), 129.0 (2C), 130.5, 131.6 (2C), 133.7, 134.8, 137.7, 139.6, 149.0, 164.0, 166.2, 166.4, 170.3, 199.9.

Trisaccharide Diol (31)

A mixture of trisaccharide (30) (392 mg, 0.278 mmol), dry CH_2Cl_2 (3 mL), and dry MeOH (3 mL) was cooled in an ice bath, and then *t*-$BuNH_2$ (295 μL, 2.78 mmol, 10 equiv.) was added dropwise with stirring. The resulting dark red solution was allowed to stand at 0°C for 5 h, then was poured into 1 M $KHSO_4$ (25 mL), and was extracted with CH_2Cl_2 (× 4). The combined organics were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash chromatography (SiO_2, 30% EtOAc/hexanes–2% MeOH) gave (31) (210 mg) as a yellow solid and a mixture of unreacted (30) and intermediate monochloroacetates, which was resubmitted to the reaction conditions for another 6 h. Workup and purification as described above gave (31) (226 mg, 65%) as a yellow *solid* (Found (FAB): $[M + Na]^+$, 1283.5. $C_{51}H_{57}Br_2IO_{15}S_2$ requires $[M + Na]^+$, 1283.8). $[\alpha]_D^{27}$ –31.5° (*c*, 0.91 in $CHCl_3$). FT–IR (thin film) 3480, 3058, 2976, 2936, 2879, 1737, 1630, 1603, 1574, 1439, 1400, 1380, 1358, 1332, 1258, 1205, 1172, 1159, 1084, 1042, 911, 814, 737, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.18, d, *J* 7.0 Hz, 3H; 1.19, d, *J* 7.0 Hz, 3H; 1.33, d, *J* 6.6 Hz, 3H; 1.33, s, 3H; 2.01, m, 1H; 2.21, m, 1H; 2.24, s, 1H; 2.39, s, 3H; 2.60, septet, *J* 7.0 Hz, 1H; 2.82, ddd, *J* 14.7, 8.4, 4.9 Hz, 1H; 3.05, ddd, *J* 16.9, 8.1, 4.0 Hz, 1H; 3.18, dd, *J* 11.0, 8.8 Hz, 1H; 3.27, dd, *J* 10.6, 8.8 Hz, 1H; 3.50–3.38, m, 6H; 3.58, dd, *J* 10.4, 7.5 Hz, 1H; 3.64, dd, *J* 11.0, 4.4 Hz, 1H; 3.78, m, 2H; 3.84, s, 1H; 4.05, s, 1H; 4.08, dd, *J* 6.8, 6.8 Hz, 1H; 4.31, d, *J* 3.3 Hz, 1H; 4.46, dd, *J* 8.4, 3.7 Hz, 1H; 4.71, d, *J* 8.8 Hz, 1H; 4.93, d, *J* 8.8 Hz, 1H; 4.96, d, *J* 7.0 Hz, 1H; 5.38, d, *J* 3.3 Hz, 1H; 6.99, s, 1H; 7.02, dd, *J* 7.0, 1.5 Hz, 1H; 7.06, m, 3H; 7.26–7.14, m, 5H; 7.39, m, 2H; 7.49, dd, *J* 8.1, 1.1 Hz, 1H; 7.53, t, *J* 7.7 Hz, 1H; 14.32, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.4, 18.8, 18.9, 21.2, 23.0, 25.9, 27.9, 32.0, 32.2, 34.1, 43.9, 54.4, 54.7, 70.2, 71.6, 71.8, 72.0, 73.8, 75.1, 75.2, 78.3, 82.6, 85.5, 102.3, 103.1, 103.7, 111.3, 116.8, 117.1, 119.2, 125.5, 126.6, 128.5 (2C), 128.9 (2C), 130.2 (2C), 130.4, 130.6 (2C), 134.8, 135.2, 137.8, 139.6, 149.0, 163.9, 170.3, 176.6, 200.0.

Tris(trimethylsilyl)silane Reduction of (31): Synthesis of Trisaccharide (32)

A solution of the diol (31) (51.0 mg, 0.040 mmol, 1 equiv.) in dry toluene (8 mL) was treated with tris(trimethylsilyl)silane (250 μL, 0.809 mmol, 20 equiv.) and Et_3B (120 μL, 0.120 mmol, 1 M in hexane). The N_2 purge was removed and 50 μL of air was injected directly into the yellow solution. The mixture was stirred at room temperature for 1 h and then diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated under vacuum, keeping the rotary evaporator bath temperature below 30°C. Purification of the crude product by flash chromatography (SiO_2; 40% EtOAc/hexanes, then 40% EtOAc/hexanes–2% MeOH) gave (32) (35.2 mg, 89%) as a yellow *foam* (Found (FAB): $[M + Na]^+$, 999.3290. $C_{51}H_{60}O_{15}S_2$ requires $[M + Na]^+$, 999.3271). $[\alpha]_D^{27}$ –46.6° (*c*, 0.70 in $CHCl_3$). FT–IR (thin film) 3436, 3058, 2976, 2934, 2879, 1766, 1738, 1631, 1574, 1440, 1400, 1380, 1359, 1331, 1204, 1158, 1117, 1071, 1026, 1000, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.18, d, *J* 7.3 Hz, 3H; 1.19, d, *J* 7.3 Hz, 3H; 1.20, s, 3H; 1.23, d, *J* 6.6 Hz, 3H; 1.30, d, *J* 5.9 Hz, 3H; 1.38, d, *J* 6.2 Hz, 3H; 1.96, dd, *J* 13.9, 4.4 Hz, 1H; 2.01, m, 1H; 2.14, dd, *J* 13.6, 2.2 Hz, 1H; 2.16, m, 1H; 2.29, s, 1H; 2.38, s, 3H; 2.61, septet, *J* 7.0 Hz, 1H; 2.79, ddd, *J* 16.7, 7.5, 4.4 Hz, 1H; 3.05, m, 1H; 3.07, dd, *J* 9.9, 9.9 Hz, 1H; 3.30–3.18, m, 4H; 3.33, dq, *J* 9.3, 6.0 Hz, 1H; 3.43, dq, *J* 9.2, 6.0 Hz, 1H; 3.46, dd, *J* 10.8, 8.2 Hz, 1H; 3.99, dq, *J* 9.2, 6.2 Hz, 1H; 4.23, s, 1H; 4.27, s, 1H; 4.37, dd, *J* 8.1, 3.7 Hz, 1H; 4.59, d, *J* 8.8 Hz, 1H; 4.64, d, *J* 9.2 Hz, 1H; 4.76, d, *J* 8.8 Hz, 1H; 4.98, dd, *J* 3.7, 2.0 Hz, 1H; 6.97, s, 1H; 7.01, d, *J* 7.0 Hz, 1H; 7.05, m, 2H; 7.12, m, 3H; 7.18, m, 2H; 7.41, d, *J* 6.6 Hz, 1H; 7.48, d, *J* 7.3 Hz, 1H; 7.52, t, *J* 7.7 Hz, 1H; 14.30, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.5, 17.6, 17.8, 18.8, 18.9, 21.2, 22.8, 25.7, 28.1, 29.7, 34.2, 42.9, 54.6, 55.8, 67.3, 70.5, 71.6, 71.7, 74.7, 75.3, 77.2, 78.7, 78.9, 83.2, 87.4, 100.6, 103.0, 103.6, 111.4, 116.9, 117.1, 119.1, 125.5, 126.4, 128.3 (2C), 128.6 (2C), 130.3 (2C), 130.5 (2C), 135.5, 136.0, 137.9, 139.6, 148.9, 163.8, 170.3, 177.3, 200.5.

RaNi Reduction of (32): Synthesis of Phenolic Acetate (33)

A flame-dried 50 mL round-bottom flask was charged with bis(phenyl sulfide) (32) (32.2 mg, 0.033 mmol) and dry THF (16 mL). About 100 pipette drops of a freshly prepared W-2 Raney nickel suspension in EtOH[33] were added. The resulting greenish-black suspension was sonicated at 40°C in a preheated bath for 30 min, with the bath temperature being maintained between 40–45°C. An additional 60 drops of Raney nickel suspension were added and the mixture was sonicated at 45°C for another 30 min. After being cooled to ambient temperature, the suspension was diluted with 3% HOAc/MeOH (20 mL), stirred vigorously, and filtered through a Celite plug, which was rinsed twice with 3% HOAc/MeOH (20 mL). The combined filtrates were concentrated to 1/4 volume, diluted with EtOAc (30 mL), and washed twice with H_2O. The combined aqueous layers were back-extracted with EtOAc. The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The resulting greenish-black residue was passed through a SiO_2 plug, with 80% EtOAc/hexanes–2% MeOH as eluent. Purification of the crude product by preparative HPLC (80% EtOAc/hexanes, 10 mm column, 5 mL min^{-1}, λ 290 nm, t_R 12.0 min) gave (33) (5.9 mg, 24%) as a yellow *glass* (Found (FAB): $[M + Na]^+$, 783.3237. $C_{39}H_{52}O_{15}$ requires $[M + Na]^+$, 783.3204). $[\alpha]_D^{27}$ –97.7° (*c*, 0.22 in $CHCl_3$). FT–IR (thin film) 3436, 3058, 2976, 2934, 2879, 1766, 1738, 1631, 1574, 1440, 1400, 1380, 1359, 1331, 1204, 1158, 1117, 1071, 1026, 1000, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.18, d, *J* 7.3 Hz, 3H; 1.19, d, *J* 7.3 Hz, 3H; 1.20, s, 3H; 1.23, d, *J* 6.6 Hz, 3H; 1.30, d, *J* 5.9 Hz, 3H; 1.38, d, *J* 6.2 Hz, 3H; 1.96, dd, *J* 13.9, 4.4 Hz, 1H; 2.01, m, 1H; 2.14, dd, *J* 13.6, 2.2 Hz, 1H; 2.16, m, 1H; 2.29, s, 1H; 2.38, s, 3H; 2.61, septet, *J* 7.0 Hz, 1H; 2.79, ddd, *J* 16.7, 7.5, 4.4 Hz, 1H; 3.05, m, 1H; 3.07, dd, *J* 9.9, 9.9 Hz, 1H; 3.30–3.18, m, 4H; 3.33, dq, *J* 9.3, 6.0 Hz, 1H; 3.43, dq, *J* 9.2, 6.0 Hz, 1H; 3.46, dd, *J* 10.8, 8.2 Hz, 1H; 3.99, dq, *J* 9.2, 6.2 Hz, 1H; 4.23, s, 1H; 4.27, s, 1H; 4.37, dd, *J* 8.1, 3.7 Hz, 1H; 4.59, d, *J* 8.8 Hz, 1H; 4.64, d, *J* 9.2 Hz, 1H; 4.76, d, *J* 8.8 Hz, 1H; 4.98, dd, *J* 3.7, 2.0 Hz, 1H; 6.97, s, 1H; 7.01, d, *J* 7.0 Hz, 1H; 7.05, m, 2H; 7.12, m, 3H; 7.18, m, 2H; 7.41, d, *J* 6.6 Hz, 1H; 7.48, d, *J* 7.3 Hz, 1H; 7.52, t, *J* 7.7 Hz, 1H; 14.30, s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.5, 17.6, 17.8, 18.8, 18.9, 21.2, 22.8, 25.7, 28.1, 29.7, 34.2, 42.9, 54.6, 55.8, 67.3, 70.5, 71.6, 71.7, 74.7, 75.3, 77.2, 78.7, 78.9, 83.2, 87.4, 100.6, 103.0, 103.6, 111.4, 116.9, 117.1, 119.1, 125.5, 126.4, 128.3 (2C), 128.6 (2C), 130.3 (2C), 130.5 (2C), 135.5, 136.0, 137.9, 139.6, 148.9, 163.8, 170.3, 177.3, 200.5.

*Aureolic Acid Analogue (6), (2*R*)-Epimer*

Phenolic acetate (33) (9.6 mg, 0.0126 mmol) was dissolved in CH_2Cl_2 (300 μL) in a 10 mL pear-shaped flask under a N_2 atmosphere. In a separate vial, *Pseudomonas fluorescens* lipase (11.9 mg) (PFL, Fluka) was dissolved in phosphate buffer (3.7 mL, pH 7, 50 mM). The PFL–buffer solution was added to the solution of (33) and the biphasic mixture was stirred vigorously at ambient temperature for 14 h. The mixture was diluted with deionized H_2O and extracted with CH_2Cl_2

(× 4). The combined organic phases were washed with H_2O and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by reverse-phase preparative HPLC using a gradient program (0–1 min 35% H_2O with 0.1% AcOH and 65% 3 : 1 CH_3CN/H_2O with 0.1% AcOH, 1–30 min linear gradient to 100% 3 : 1 CH_3CN/H_2O with 0.1% AcOH, 5 mL min^{-1}, t_R 22.1 min). The CH_3CN was removed under vacuum, and the aqueous phase was extracted with CH_2Cl_2 (× 4). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, concentrated, and dried by co-evaporation twice from benzene to give analogue (6) (8.5 mg, 95%) as a dark yellow *glass* (Found (FAB): $[M+Na]^+$, 741.3091. $C_{37}H_{50}O_{14}$ requires $[M+Na]^+$, 741.3098). $[\alpha]_D^{25}$ –46.7° (*c*, 0.85 in $CHCl_3$). FT–IR (thin film) 3412, 3065, 2975, 2934, 2879, 2245, 1732, 1634, 1604, 1582, 1450, 1416, 1385, 1345, 1310, 1250, 1162, 1127, 1069, 1022, 908, 733 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.20, d, *J* 7.1 Hz, 3H; 1.21, d, *J* 6.8 Hz, 3H; 1.23, d, *J* 5.9 Hz, 3H; 1.33, d, *J* 6.1 Hz, 3H; 1.35, s, 3H; 1.38, d, *J* 6.1 Hz, 3H; 1.69, ddd, *J* 12.0, 10.3, 10.3 Hz, 1H; 1.83, ddd, *J* 12.2, 10.0, 10.0 Hz, 1H; 2.00, dd, *J* 13.8, 4.3 Hz, 1H; 2.05, dd, *J* 13.8, 2.1 Hz, 1H; 2.28–2.17, m, 3H; 2.38, m, 1H; 2.42, br s, 1H; 2.64, septet, *J* 7.1 Hz, 1H; 2.98, ddd, *J* 10.6, 4.3, 4.3 Hz, 1H; 3.11, t, *J* 8.5 Hz, 1H; 3.14, t, *J* 8.8 Hz, 1H; 3.19, ddd, *J* 16.6, 5.1, 5.1 Hz, 1H; 3.26, dq, *J* 9.3, 6.1 Hz, 1H; 3.35, dq, *J* 9.2, 6.1 Hz, 1H; 3.48, ddd, *J* 11.7, 8.2, 5.0 Hz, 1H; 3.52, ddd, *J* 11.8, 8.4, 5.3 Hz, 1H; 3.99, dq, *J* 9.5, 6.2 Hz, 1H; 4.05, d, *J* 1.2 Hz, 1H; 4.46, s, 1H; 4.54, dd, *J* 9.9, 1.8 Hz, 1H; 4.59, d, *J* 9.5 Hz, 1H; 4.60, dd, *J* 10.0, 4.2 Hz, 1H; 4.72, dd, *J* 9.8, 2.0 Hz, 1H; 5.00, dd, *J* 4.2, 2.0 Hz, 1H; 6.84, d, *J* 7.6 Hz, 1H; 6.99, s, 1H; 7.12, d, *J* 7.6 Hz, 1H; 7.48, t, *J* 7.9 Hz, 1H; 9.63, s, 1H; 15.62, br s, 1H. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.7, 17.8, 17.9, 18.9, 19.0, 23.0, 26.7, 28.9, 34.2, 37.1, 37.4, 43.9, 66.6, 70.6, 72.1, 72.3, 74.8, 75.2, 79.5, 80.8, 82.3, 94.8, 97.1, 97.2, 99.6, 109.8, 110.9, 112.5, 117.3, 118.1, 132.8, 136.5, 139.4, 157.9, 165.7, 177.5, 201.1.

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