at room temperature. After 60 h the mixture was diluted with methanol (10 mL) and saturated again with SO_2 to generate a white precipitate that was collected by centrifuging (2000 rpm × 10 min). The white solid obtained was suspended in 10 mL of methanol–ether (1:10), recentrifuged, and dried in vacuo to give crystals of **20** (43 mg, 63%): mp 140–145 °C dec (lit.[2] mp 145–147 °C dec); ^{1}H NMR (400 MHz, D_2O) δ $Me_3Si(CH_2)_3SO_3Na$ (0.015 ppm) 3.29 (1 H, ddd, J = 9.6, 4.6, 3.0 Hz, H-5), 3.61 (1 H, dd, J = 9.3, 9.0 Hz, H-3), 3.72 (1 H, dd, J = 9.6, 9.3 Hz, H-4), 3.94 (1 H, dd, J = 10.4, 9.0 Hz, H-2), 3.95 (1 H, dd, J = 12.9, 4.6 Hz, H-6), 4.03 (1 H, dd, J = 12.9, 3.0 Hz, H-6), 4.19 (1 H, d, J = 10.4 Hz, H-1); ^{13}C NMR [D_2O with $Me_3Si(CH_2)_3SO_3Na$ as internal standard] carbons with 1 proton attached δ 63.04, 69.99, 72.11, 73.20, 78.62, carbon with 2 protons attached δ 60.27; mass spectrum, m/e (relative intensity) 227 (5), 143 (24), 125 (75), 124 (85), 96 (100).

(+)-Nojirimycin (1). A solution of **20** (30 mg, 0.115 mmol) in water (1 mL) was applied to a column of 10 mL of Dowex 1×2 (OH^-) resin (100–200 mesh) and eluted with water (200 mL). The elute was lyophilized to give 1 (20 mg, 90%) as a white crystalline product: mp 124–131 °C dec (lit.[2] mp 125–131 °C dec); $[\alpha]^{24}_D$ +71.2° (c 0.17, H_2O, equilibrium) [lit.[2] $[\alpha]^5_D$ +73.5° (H_2O, 20 h)].

Registry No. 1, 15218-38-9; 2, 19130-96-2; 3, 50622-09-8; 4, 108817-96-5; 5, 108817-97-6; (*E*)-6, 108817-98-7; (*Z*)-6, 108818-11-7; 7, 108817-99-8; 8, 108818-00-4; 9, 108818-01-5; 10, 108818-02-6; 11, 108818-03-7; 12, 108818-04-8; 13, 108818-05-9; 14, 108818-06-0; 15, 108818-07-1; 16, 108818-08-2; 17, 108818-09-3; 18, 108818-10-6; 20, 81703-56-2; [(ethoxycarbonyl)methylene]triphenylphosphorane, 1099-45-2; trimethyl phosphonoacetate, 5927-18-4; *p*-methoxybenzyl *S*-(4,6-dimethylpyrimidin-2-yl)thiocarbonate, 41840-29-3.

Stereodivergent Total Synthesis of *N*-Acetylacosamine and *N*-Benzoylristosamine

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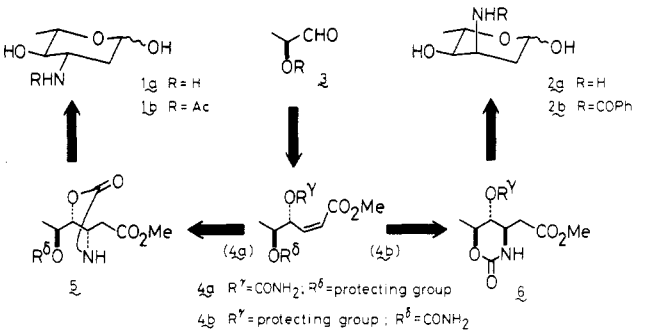
Highly diastereoselective syntheses of L-*N*-acetylacosamine (**1b**) and L-*N*-benzoylristosamine (**2b**), two isomeric L-3-amino-2,3,6-trideoxyhexoses, were achieved by utilizing the intramolecular conjugate addition of carbamate group in the *Z*-α,β-unsaturated esters **4a** and **4b**, respectively. **4a** and **4b** were prepared from the common intermediate, 4,5-dihydroxy-2-hexynoate derivative **7a**, readily available by the non-chelation-controlled addition of methyl propiolate to *O*-(*tert*-butyldimethylsilyl)lactaldehyde **3**.

The 3-amino-2,3,6-trideoxyhexoses are distributed in nature as the glycosidic moiety of important antibiotics. Daunosamine is found in anthracycline antibiotics such as adriamycin and daunorubicin,[1] used clinically in antitumor therapy. A clinically important modification of adriamycin is the replacement of daunosamine for its C-4 epimer, acosamine (**1a**), and it is reported to reduce the relative cardiotoxicity.[2] The acosamine was originally isolated as one of the sugar constituents of actinoidin,[3] a member of the important vancomycin group of glycopeptide antibiotics. Another naturally occurring isomer is ristosamine (**2a**), which is also a carbohydrate constituent of vancomycin group antibiotics such as ristomycin.[4] Although a variety of efforts[5] to synthesize these amino sugars have been reported, to our knowledge, there is not a stereocontrolled divergent synthesis of these isomeric sugars from common intermediate without the aid of stereochemical inversion procedures. Recently we have developed a new amination methodology using the intramolecular conjugate additions of γ- or δ-carbamoyloxy-α,β-unsaturated esters.[6] They provide a good way to achieve diastereoselective amination of acyclic olefinic systems, since complementary diastereofacial selection can be accomplished by changing the site of carbamoyloxy group between γ- and δ-positions. Its synthetic utility has been demonstrated by the stereoselective syntheses of all four possible diastereomers of racemic *N*-acyl-3-amino-2,3,6-trideoxyhexose.[7,8] The relatively low selectivity in the conjugate addition of the homoallylic carbamate in the synthesis of (±)-*N*-benzoyldaunosamine[8] was dramatically improved by using *Z*-α,β-unsaturated ester instead of the *E* isomer (eq 1), and hence L-*N*-benzoyldaunosamine was synthesized under high stereocontrol.[9,10] In this paper we

Scheme I



(1) Arcamone, F.; Franceschi, G.; Orezzi, P.; Babier, W.; Mondelli, R. *J. Am. Chem. Soc.* **1964**, *86*, 5334. Arcamone, F.; Cassinelli, G.; Orezzi, P.; Franceschi, G.; Mondelli, R. *Ibid.* **1964**, *86*, 5335; Arcamore, F.; Franceschi, G.; Penco, S.; Selva, A. *Tetrahedron Lett.* **1969**, 1007.

(2) Marco, A. D.; Casazza, A. M.; Dasdia, T.; Formelli, F.; Necco, A.; Soranzo, C. *J. Med. Chem.* **1975**, *18*, 703.

(3) Sztaricskai, F.; Harris, C. M.; Harris, T. M. *Tetrahedron Lett.* **1979**, 2861.

(4) Bognar, R.; Sztaricskai, F.; Munk, M. E.; Tamas, J. *J. Org. Chem.* **1974**, *39*, 2971. Hunt, A. H.; Debono, M.; Merkel, K. E.; Barnhart, M. *Ibid.* **1984**, *49*, 635.

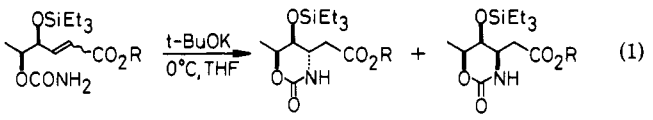
(5) For comprehensive review on syntheses of 2,3,6-trideoxy-3-aminohexoses, see: Hauser, F. M.; Ellenberger, S. R. *Chem. Rev.* **1986**, *86*, 35.

(6) Hirama, M.; Shigemoto, T.; Yamazaki, Y.; Itô, S. *J. Am. Chem. Soc.* **1985**, *107*, 1797.

(7) Hirama, M.; Shigemoto, T.; Yamazaki, Y.; Itô, S. *Tetrahedron Lett.* **1985**, *26*, 4133.

(8) Hirama, M.; Shigemoto, T.; Itô, S. *Tetrahedron Lett.* **1985**, *26*, 4137.

0022-3263/87/1952-3342$01.50/0



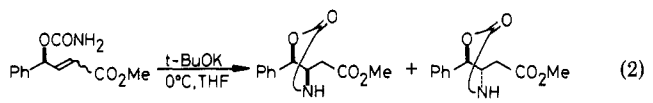
2,3-E(R=Et)	5	:	1
2,3-Z(R=Me)	>100	:	1

describe the further development of our divergent route to L-*N*-acetylacosamine (**1b**) and L-*N*-benzoylristosamine (**2b**) from L-lactaldehyde (**3**) via *Z* olefin **4** (Scheme I).

L-*N*-Acetylacosamine. The erythro-diol derivative **7a**, common intermediate for **4a** and **4b**, was prepared by the coupling of *O*-(*tert*-butyldimethylsilyl)lactaldehyde **3** and methyl propiolate with LDA as described previously.[9] Pure **7a** was isolated by column chromatography in 50–60% yield. Attempts to improve the Cram selectivity (**7a**/threo isomer ≈ 5:1) by changing the protecting group were unsuccessful. Unexpectedly, sterically more demanding groups tend to give lower selectivity ($SiEt_3$, 3.5:1; $SiPh_2$-*t*-Bu, 2:1). Furthermore, since a less chelating metal ion was expected to improve the Cram selectivity, bases such as KDA were examined as well as additives such as $TiCl_4$–$Ti(O\text{-}i\text{-}C_3H_7)_4$,[11] but all resulted in unsatisfactory selectivity and yield.

The silyl ether **7a** was hydrolyzed to the diol **7b** (86%) and reacted with a small excess of chlorosulfonyl isocyanate followed by partial hydrolysis in water to give biscarbamate **7c** in 71% yield. Controlled hydrogenation of alkyne **7c** with Lindlar catalyst gave the cis olefin **4a** in 94% yield. A trace of saturated ester, which could be removed by HPLC but not by recrystallization, was often detected by NMR spectroscopy in the reaction mixture. Such purification, however, was not necessary for the synthetic purpose, since the contaminate derived from the saturated ester was readily removable at the lactone stage by conventional chromatography.

We expected that **4a** should exhibit much higher 1,2-syn stereoselectivity in the intramolecular conjugate addition than *E* isomer (>20:1), due to the steric effect ($A^{1,3}$ strain),[8,12] as exemplified in eq 2.[6] However, it is not easy



11 2,3-E	12	:	1
12 2,3-Z	>100	:	1

to anticipate the effect of the olefin geometry on the preference of the desired attack of the allylic carbamate group over the homoallylic group, although much faster reaction of the former was observed in the (*E*)-enoate series.[6-8] Under the standard conditions (1 equiv of *t*-BuOK, 0 °C, 20 min),[9] **4a** cyclized smoothly to afford trans oxazolidinone **5**, 3,4-syn amino alcohol derivative, in 90% yield. The selectivity was evaluated to be >40:1 by 400-MHz ^1H NMR spectroscopy, apparently higher than the *E* series,[7,8] although the structural and stereostructural assignment of a trace of isomers has not been made. Conversion of **5** to **1b** followed the procedure previously established for the racemic compound.[7] Alkaline hydrolysis of both the carbamate and ester group, evaporation of the volatiles, and lactonization with acetic anhydride were performed in one pot to give a 3:1 mixture of δ-lactone **8** and γ-lactone **9** in 82% yield after chromatography (Scheme II). The combined lactone mixture was reduced with 2 molar equiv of DIBAL at low temperature to give acetoxypyranose **10**. Attempted direct removal of the *O*-acetyl group by using excess DIBAL failed because of the concomitant reduction of hemiacetal. Thus, the remaining acetate group was hydrolyzed with 1 M NaOH/MeOH and purified by chromatography to afford crystalline L-*N*-acetylacosamine (**1b**), mp 184–187 °C (AcOEt), $[\alpha]^{25}_D$ −18° (constant after 3 h), in 87% yield. The optical rotation and IR and ^1H NMR spectral data are identical with those reported by Dyong.[13]

L-*N*-Benzoylristosamine. The synthesis of L-ristosamine (**2a**) requires the regiocontrolled protection of the diol **7b** as homoallylic carbamate **7g**. The protection of free hydroxyl group of **7a** as THP ether and subsequent deprotection of silyl ether with *n*-Bu_4NF gave the homoallylic alcohol **7e** (74% yield from **7a**). Treatment of **7e** with $ClSO_2NCO$ followed by partial hydrolysis with water afforded the monocarbamate **7f** in 87% yield, achieving the carbamation of homoallylic alcohol group and deprotection of the THP ether in one pot. The hydroxyl group of **7f** was reprotected with chlorotriethylsilane to give **7g** (73% yield). The THP group was replaced by triethylsilyl for two reasons: (1) the additional chiral center due to

Scheme II

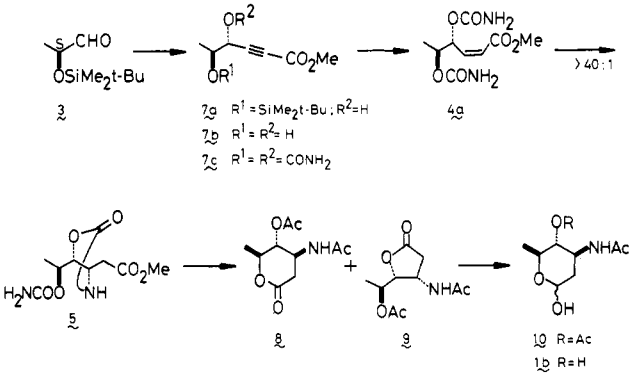
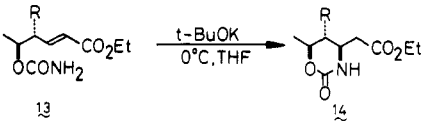


Table I

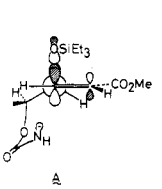


R		R	
H[a]	10:1[b]	OAc	19:1[b]
O-*t*-Bu	7:1[b]	$OSiMe_2$-*t*-Bu	36:1[b]
OMe	18:1	$OSiEt_3$	>50:1[c]

[a] Methyl ester instead of ethyl was used. [b] See ref 6. [c] See ref 7.

(9) Hirama, M.; Nishizaki, I.; Shigemoto, T.; Itô, S. *J. Chem. Soc., Chem. Commun.* **1986**, 393.

(10) As reported previously,[9] the higher asymmetric induction in *Z* olefin is explained by considering the rigid transition state A adequate for the antiperiplanar effect due to allylic C–O. Its conformation is constrained by severe $A^{1,3}$ strain; the allylic conformation of *E* olefin is much more flexible so that the antiperiplanar effect functions to a lesser extent.



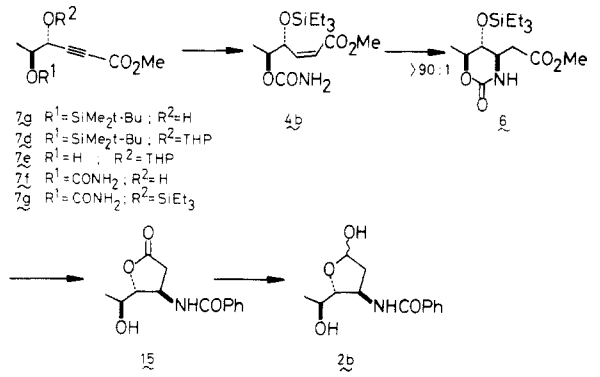
A

(11) Tabusa, F.; Yamada, T.; Suzuki, K.; Mukaiyama, T. *Chemistry Lett.* **1984**, 405. Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556.

(12) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

(13) Dyong, I.; Bendlin, H. *Chem. Ber.* **1978**, *111*, 1677.

Scheme III



THP would complicate the evaluation of diastereofacial selectivity in the following intramolecular conjugate addition; (2) in our previous study[7] of the effect of γ-substituents on the diastereofacial selectivity in the conjugate addition of homoallylic carbamate to *E* olefin **13**, the triethylsilyl ether showed the highest selectivity as listed in Table I.[14,15]

Catalytic hydrogenation of **7g** with Lindlar catalyst in MeOH afforded homogeneous *Z* olefin **4b** in 97% yield. No epimerization of the allylic center was detected by NMR. The carbamate **4b** was treated with *t*-BuOK under the standard conditions to give the desired 1,3-syn (1,2-anti) product **6** exclusively (73%) as expected (Scheme III). Alkaline hydrolysis of **6** and subsequent benzoylation of the reaction mixture as in the synthesis of racemic compounds[7] resulted in the formation of the known γ-lactone benzoyl amide **15**.[16] Reduction of **15** with excess DIBAL at low temperature afforded L-*N*-benzoylristosamine (**2b**), mp 132–134 °C, $[\alpha]^{23}_D$ −10° (10 min), −24° (3 h, constant), in 65% yield. The ^{1}H NMR spectral data of **2b** in Me_2SO-d_6 are in good agreement with those of furanose structure reported by Fuganti.[16]

Experimental Section

^{1}H NMR spectra were run for $CDCl_3$ solutions, unless otherwise stated, at 90, 200, and 400 MHz on JEOL FX-90Q, Varian XL-200, and JEOL GX-400 instruments. Chemical shifts are reported in δ values (ppm) relative to internal tetramethylsilane. Infrared spectra were measured on a JASCO IRA-2 spectrometer and expressed in reciprocal centimeters. Optical rotations were recorded on a Perkin-Elmer 141 polarimeter using 1- or 5-cm^3 capacity quartz cell (10-cm path length). Melting points were measured on a Yanaco MP-S3 hot stage melting point apparatus and were uncorrected. Elemental analyses were performed at Instrumental Analysis Center for Chemistry, Tohoku University.

THF was distilled from sodium benzophenone ketyl. CH_2Cl_2 was dried over anhydrous $CaCl_2$ or dried by passing through activated alumina (200 mesh) column.

Analytical thin-layer chromatography (TLC) was performed by using plates precoated with Wako silica gel 70 F_{254} (0.25 mm thick). Merck silica gel 60 (70–230 mesh) was used for column chromatography. HPLC analysis was performed on a GILSON HPLC system (Model 302-802) with ERC-7510 RI detector and Shimazu Chromatopac C-R3A.

(*S*)-2-[(*tert*-Butyldimethylsilyl)oxy]propanal (3). (*S*)-(−)-Ethyl lactate (4.104 g, 34.7 mmol) was stirred with TBDMSCl (5.50 g, 36.5 mmol) and imidazole (4.994 g, 73.4 mmol) in dry DMF (8 mL) at room temperature overnight. The mixture was directly chromatographed (silica gel, 100 g; 10:1 hexane–ether) to give 8.056 g (100%) of (*S*)-ethyl *O*-(*tert*-butyldimethylsilyl)lactate as a colorless oil: $[\alpha]^{20}_D$ −31.3°; ^{1}H NMR (90 MHz) 0.03 (3 H, s), 0.06 (3 H, s), 0.86 (9 H, s), 1.23 (3 H, t, *J* = 7.0 Hz), 1.35 (3 H, d, *J* = 6.8 Hz), 4.13 (2 H, q, *J* = 7.0 Hz), 4.26 (1 H, q, *J* = 6.8 Hz); IR (film) 2985, 2960, 2940, 2900, 2865, 1756, 1734, 1474, 1462, 1442, 1386, 1370, 1362, 1256, 1190, 1146, 1108, 1058, 1024, 976, 936, 890, 862, 832, 810, 778, 660. Anal. Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found: C, 57.15; H, 10.43.

To the ethyl ester (7.298 g, 31.4 mmol) in dry CH_2Cl_2 (60 mL) was added dropwise 31.4 mL of 1 M hexane solution of DIBAL at −78 °C under Ar. Stirring was continued for further 20 min, then 5 mL of MeOH was added dropwise at the same temperature. After being stirred at room temperature for 30 min, the resulting slurry was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (silica gel, 100 g; 25:1 hexane–ether) gave **3** (oil, 4.447 g, 75%): $[\alpha]^{19}_D$ −12.0° (*c* 1.51, $CHCl_3$); ^{1}H NMR (90 MHz) 0.10 (6 H, s), 0.92 (9 H, s), 1.27 (3 H, d, *J* = 7.0 Hz), 4.09 (1 H, dq, *J* = 1.3, 7.0 Hz), 9.60 (1 H, d, *J* = 1.3 Hz); IR (film) 2970, 2945, 2900, 2870, 2810, 2705, 1738, 1474, 1462, 1444, 1404, 1386, 1370, 1360, 1254, 1100, 1004, 962, 936, 836, 810, 776, 680, 662. Anal. Calcd for $C_9H_{20}O_2Si$: C, 57.39; H, 10.70. Found: C, 57.97; H, 10.81.

(4*R*,5*S*)-Methyl 5-[(*tert*-Butyldimethylsilyl)oxy]-4-hydroxy-2-hexynoate (7a). Methyl propiolate (2.8 mL, 31.5 mmol) was added dropwise to a solution of LDA, prepared from diisopropylamine (6.3 mL, 36.2 mmol) and 1.5 M hexane solution of *n*-BuLi (23 mL, 34.5 mmol) in dry THF (60 mL), at −78 °C under Ar over a period of 10 min. After 30 min, a solution of **3** (3.993 g, 21.2 mmol) in dry THF (20 mL) was added dropwise, and the mixture was stirred at the same temperature for 25 min, followed by the addition of acetic acid (1.5 mL) in dry THF (9 mL). The mixture was poured into 900 mL of a vigorously stirred saturated aqueous solution of NH_4Cl and extracted with ether: the addition of acetic acid may be omitted, but aqueous NH_4Cl solution must not be added to the reaction mixture.[9] The dried organic layer was concentrated and the residue was chromatographed on silica gel (100 g) column with 20:1 → 10:1 hexane–ether as eluent, affording 0.379 g (10%) of recovered **3**, 1.715 g (30%) of ca. 1:1 mixture of **7a** and its threo isomer, 1.026 g (18%) of >10:1 mixture, and 1.755 g (30%) of pure **7a**. Repeated chromatography of the mixture gave additional 1.160 g (20%) of **7a**. The ratio of **7a** and its threo isomer was determined by HPLC (column: DEVELOSIL 30-3, 25 cm × 4.6 mm; 5:1 hexane–AcOEt; 1.0 mL/min; RI detector; t_R of **7a** = 7.9 min, t_R of the threo isomer = 8.8 min) or by NMR spectroscopy: the doublet signal (~2.6 ppm, *J* = 6.4 Hz) of the hydroxyl proton of **7a** in the spectrum of the mixture always appeared upfield by 0.1–0.2 ppm to that of the threo isomer (doublet, *J* = 6.6 Hz). **7a** (colorless oil): $[\alpha]^{18}_D$ 0.84° (*c* 4.28, $CHCl_3$); ^{1}H NMR (90 MHz) 0.11 (6 H, s), 0.91 (9 H, s), 1.25 (3 H, d, *J* = 6.2 Hz), 2.75 (1 H, d, *J* = 6.4 Hz, OH), 3.77 (3 H, s), 3.97 (1 H, dq, *J* = 4.4, 6.2 Hz), 4.33 (1 H, dd, *J* = 4.4, 6.4 Hz); IR (film) 3450, 2950, 2930, 2900, 2855, 2250, 1710, 1464, 1436, 1376, 1254, 1135, 1112, 1092, 837, 776. Anal. Calcd for $C_{13}H_{24}O_4Si$: C, 57.32; H, 8.88. Found: C, 57.54; H, 8.93.

(4*R*,5*S*)-Methyl 4,5-Dihydroxy-2-hexynoate (7b). A solution of **7a** (1.026 g) in 18 mL of 1:1:1 THF–water–AcOH was stirred at 60 °C overnight. Saturated aqueous NH_4Cl was added, and the mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on column chromatography (silica gel, 25 g; 1:2 hexane–ether) to give colorless oil **7b** (524 mg, 88%): $[\alpha]^{30}_D$ −17.8° (*c* 3.95, $CHCl_3$); ^{1}H NMR (90 MHz, $CDCl_3$–D_2O) 1.29 (3 H, d, *J* = 6.5 Hz), 3.79 (3 H, s), 3.98 (1 H, dq, *J* = 3.4, 6.5 Hz), 4.43 (1 H, *J* = 3.4 Hz); IR (film) 3320, 2950, 2230, 1700, 1436, 1245, 1028, 1066, 1034, 992, 947, 919, 848, 804, 750. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.91; H, 6.58.

(4*R*,5*S*)-Methyl 4,5-Bis[(carbamoyl)oxy]-2-hexynoate (7c). Chlorosulfonyl isocyanate (0.80 mL, 9.2 mmol) was added dropwise to a stirred solution of **7b** (481 mg, 3.04 mmol) in dry CH_2Cl_2 (10 mL) at −20 °C under Ar. After 30 min water (50 mL) was added, and the mixture was heated at 60 °C for 30 min without cooling condenser to evaporate CH_2Cl_2. The water layer was saturated

(14) We have explained this γ-substituted effect by the combination of steric and stereoelectronic effects (antiperiplanar effect)[8] instead of electrostatic interaction, on the assumption that the C–O σ* of silyl ethers as well as acetate is lower than that of the alkyl ether (see the similar discussion by Keck: Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 265), which is, however, still requiring the theoretical confirmation.

(15) Triethylsilyl group is sterically more demanding than *tert*-butyldimethylsilyl: see footnote 9 in ref 7.

(16) Fronza, G.; Fuganti, C.; Grasselli, P. *Tetrahedron Lett.* **1980**, *21*, 2999; *J. Chem. Soc., Perkin Trans 1* **1982**, 885.

with NaCl and extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$ and NH_4Cl, dried over $MgSO_4$, and concentrated. The solid residue was recrystallized from AcOEt–hexane to give crystalline biscarbamate **7c** (529 mg, 71%): mp 162–165 °C; $[\alpha]^{30}_D$ –75.5° (*c* 2.25, MeOH); ^1H NMR (90 MHz, acetone-d_6) 1.30 (3 H, d, *J* = 6.6 Hz), 3.77 (3 H, s), 4.97 (1 H, dq, *J* = 3.8, 6.6 Hz), 5.53 (1 H, d, *J* = 3.8 Hz), 5.91 (2 H, br, NH_2), 6.15 (2 H, br, NH_2); IR (KBr) 3505, 3400, 3350, 3190, 2985, 2945, 2230, 1735, 1705, 1615, 1598, 1437, 1395, 1375, 1344, 1320, 1304, 1290, 1265, 1190. Anal. Calcd for $C_9H_{12}N_2O_6$: C, 44.27; H, 4.95; N, 11.47. Found: C, 44.17; H, 5.01; N, 11.41.

(4*R*,5*S*)-Methyl (*E*)-4,5-Bis[(carbamoyl)oxy]-2-hexynoate (4a). A solution of **7c** (52 mg) in MeOH (2 mL) was stirred at room temperature under H_2 (1 atm) with 5% Pd on $CaCO_3$ (2 mg) poisoned with lead. The reaction was carefully monitored by TLC. After 20 min, **7c** (R_f 0.70, AcOEt) disappeared, the mixture was immediately filtered through Celite, and the filtrate was concentrated. The solid residue was recrystallized from AcOEt–hexane to yield **4a** as a colorless powder (49 mg, 94%; R_f 0.50, AcOEt): mp 115–117 °C; ^1H NMR (400 MHz, acetone-d_6) 1.16 (3 H, d, *J* = 6.5 Hz), 3.69 (3 H, s), 5.00 (1 H, dq, *J* = 3.3, 6.5 Hz), 5.86 (4 H, br, NH_2), 5.96 (1 H, d, *J* = 11.3 Hz), 6.14 (1 H, dd, *J* = 8.7, 11.3 Hz), 6.23 (1 H, dd, *J* = 3.3, 8.7 Hz); IR (KBr) 3500, 3450, 3360, 3330, 1718, 1682, 1610, 1580, 1400, 1332, 1238, 1220, 1180, 1145, 1085, 1060, 1048, 1036, 836. Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.90; H, 5.73; N, 11.38. Found: C, 43.78; H, 5.84; N, 11.34. A trace of the saturated ester was often detected by ^1H NMR spectroscopy (acetone-d_6): 1.19 (3 H, d, *J* = 6.2 Hz), 1.99 (2 H, m), 2.37 (2 H, t, *J* = 7.5 Hz), 3.63 (3 H, s), 4.80 (2 H, m) 5.93 (4 H, br).

(4*S*,5*R*,1′*S*)-5-[1′-((Carbamoyl)oxy)ethyl]-4-[(methoxycarbonyl)methyl]-2-oxazolidinone (5). To a stirred suspension of *t*-BuOK (44 mg, 0.39 mmol) in dry THF (10 mL) was added quickly a solution of **4a** (93 mg, 0.38 mmol) in dry THF (5 mL) at 0 °C under Ar. After 20 min, saturated aqueous NH_4Cl (0.2 mL) was added, and the mixture was stirred vigorously for 5 min and filtered through sintered glass. The filtrate was concentrated in vacuo. The residual solid was recrystallized from AcOEt to afford **5** (83 mg, 90%) as colorless needles: mp 152–154 °C; $[\alpha]^{25}_D$ –80° (*c* 0.2, MeOH); ^1H NMR (400 MHz, acetone-d_6) 1.25 (3 H, d, *J* = 6.7 Hz), 2.57 (1 H, dd, *J* = 8.0, 16.7 Hz), 2.64 (1 H, dd, *J* = 6.0, 16.7 Hz), 3.54 (3 H, s), 3.92 (1 H, ddd, *J* = 5.5, 6.0, 8.0 Hz), 4.19 (1 H, dd, *J* = 4.5, 5.5 Hz), 4.76 (1 H, dq, *J* = 4.5, 6.7 Hz), 5.83 (2 H, br, NH_2), 6.63 (1 H, br, NH); IR (KBr) 3450, 3350, 3310, 3210, 2980, 2950, 2920, 1755, 1720, 1695, 1615, 1450, 1435, 1395, 1374, 1335, 1315, 1272, 1235, 1200, 1142, 1115, 1088, 1052, 1010, 995, 940. Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.90; H, 5.73; N, 11.38. Found: C, 43.91; H, 5.69; N, 11.13. In the crude residue, two triplet signals probably due to H-2 of isomers were detected at 4.41 (t, *J* = 8.5 Hz) and 4.50 ppm (t, *J* = 9.5 Hz) by 400-MHz ^1H NMR spectroscopy besides that of **5** (4.19 ppm) in the ratio of 1.8:2.2:96.0.

(3*S*,4*R*,5*S*)-3-Acetamido-4-acetoxy-5-hexanolide (8) and (3*S*,4*R*,5*S*)-3-Acetamido-5-acetoxy-4-hexanolide (9). A solution of **5** (54 mg, 0.22 mmol) in EtOH (2 mL) was stirred at 60 °C with 1 mL of 1 N aqueous NaOH for 12 h. After the solution was concentrated under reduced pressure, 3 mL of Ac_2O was added, and the suspension was stirred at room temperature for 12 h and then at 60 °C for 1.5 h. The mixture was diluted with saturated aqueous NH_4Cl and extracted with AcOEt. The dried organic extracts were concentrated and chromatographed (silica gel, 2:1 AcOEt–CH_2Cl_2) to give a solid mixture of **8** and **9** (3:1, 41 mg, 82%). On a routine basis this mixture was used directly in the next step. An analytical sample of **8**, however, was obtained by careful chromatographic separation or recrystallization of the mixture; further isolation of **9** has not been attempted. **8** (colorless powder): mp 159–160 °C (AcOEt–hexane); $[\alpha]^{25}_D$ –74.1° (*c* 1.36, EtOH); ^1H NMR (90 MHz) 1.39 (3 H, d, *J* = 6.2 Hz), 1.96 (3 H, s), 2.13 (3 H, s), 2.57 (1 H, dd, *J* = 7.7, 17.4 Hz), 3.11 (1 H, dd, *J* = 6.8, 17.4 Hz), 4.39 (1 H, dq, *J* = 9.0, 6.2 Hz), 4.43 (1 H, ddt, *J* = 7.7, 8.4, 6.8 Hz), 4.78 (1 H, dd, *J* = 8.4, 9.0 Hz), 6.00 (1 H, br d, *J* = 6.8 Hz); IR (KBr) 3350, 2950, 1738, 1706, 1630, 1540, 1415, 1362, 1302, 1285, 1265, 1230, 1190, 1150, 1125, 1095, 1070, 1045, 970, 955, 882, 755. Anal. Calcd for $C_{10}H_{15}NO_5 \cdot H_2O$: C, 48.58; H, 6.93; N, 5.67. Found: C, 48.48; H, 7.12; N, 5.51. **9**: ^1H NMR (90 MHz) 1.39 (3 H, d, *J* = 6.5 Hz), 1.97 (3 H, s), 2.07 (3 H, s), 2.48 (1 H, dd, *J* = 2.2, 18.5 Hz), 2.95 (1 H, dd, *J* = 7.4, 18.5 Hz), 4.43 (1 H, dd, *J* = 5.0, 8.6 Hz), 5.04 (1 H, ddd, *J* = 2.2, 5.0, 7.4 Hz), 5.17 (1 H, dq, *J* = 8.6, 6.5 Hz), 6.3 (1 H, br, NH); IR ($CHCl_3$) 1782 (8, 1734).

***N*-Acetylacosamine (1b).** To a stirred solution of the mixture of **8** and **9** (21 mg, 0.091 mmol) in dry THF (3 mL) was added dropwise 0.185 mL of 1 M DIBAL in hexane at –78 °C under Ar atmosphere. After the solution was stirred at –50 °C for 1 h, 0.1 mL of MeOH was added, and the mixture was stirred at room temperature for 30 min and filtered through Celite. The filtrate was concentrated under reduced pressure, to the residue were added MeOH (2 mL) and 1 M aqueous NaOH (1 mL), and the mixture was stirred at room temperature for 4 h. After being stirred with 2 mL of AcOEt for 30 min, the mixture was concentrated, and the residue was chromatographed on silica gel (1 g) column with AcOEt as eluent to afford crystalline **1b** (15 mg, 87%): mp 184–187 °C (AcOEt–hexane): $[\alpha]^{25}_D$ –21° (after 10 min), –18° (after 3 h, constant) (*c* 0.41, H_2O); ^1H NMR (400 MHz, D_2O, 2:3 mixture of α- and β-anomers of pyranose after 20 h) [α-anomer] 1.28 (3 H, d, *J* = 6.4 Hz, H6), 1.73 (1 H, ddd, *J* = 3.7, 12.7, 13.8 Hz, H2), 2.01 (3 H, s, Ac), 2.04 (1 H, ddd, *J* = 1.2, 4.7, 13.8 Hz, H2), 3.18 (1 H, dd, *J* = 9.7, 10.0 Hz, H4), 3.98 (1 H, dq, *J* = 9.7, 6.4 Hz, H5), 4.13 (1 H, ddd, *J* = 4.7, 10.0, 12.7 Hz, H3), 5.30 (1 H, dd, *J* = 1.2, 3.7 Hz, H1), [β-anomer] 1.30 (3 H, d, *J* = 6.3 Hz, H6), 1.49 (1 H, dt, *J* = 10.0, 12.7 Hz, H2), 2.01 (3 H, s, Ac), 2.17 (1 H, ddd, *J* = 2.0, 4.8, 12.7 Hz, H2), 3.13 (1 H, dd, *J* = 9.3, 10.0 Hz, H4), 3.53 (1 H, dq, *J* = 9.3, 6.3 Hz, H5), 3.90 (1 H, ddd, *J* = 4.8, 10.0, 12.7 Hz, H3), 4.97 (1 H, dd, *J* = 2.0, 10.0 Hz, H1); IR (KBr) 3370, 3280, 3095, 2970, 2915, 2900, 2850, 1638, 1556, 1445, 1425, 1378, 1330, 1310, 1258, 1156, 1116, 1088, 1072, 1046, 988, 966.

(4*R*,5*S*)-Methyl 5-[(*tert*-Butyldimethylsilyl)oxy]-4-(2′-tetrahydropyranyloxy)-2-hexynoate (7d). To a stirred solution of **7a** (1.755 g, 6.44 mmol) and 10 mg of *p*-TsOH in CH_2Cl_2 (60 mL) was added dropwise dihydropyran (1.2 mL, 13.2 mmol) in CH_2Cl_2 (10 mL) at room temperature over a period of 12 min. After 1 h the solution was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and NH_4Cl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel column (25 g) with 20:1 hexane-ether as eluent to afford 2.287 g (99.5%) of colorless oil **7d** as 3:1 mixture of diastereomers: $[\alpha]^{35}_D$ –69.2° (*c* 4.62, $CHCl_3$); ^1H NMR (90 MHz) [major isomer] 0.09 (3 H, s), 0.10 (3 H, s), 0.90 (9 H, s), 1.27 (3 H, d, *J* = 6.2 Hz), 1.65 (6 H, m), 3.6 (2 H, m), 3.76 (3 H, s), 3.99 (1 H, dq, *J* = 5.5, 6.2 Hz), 4.33 (1 H, d, *J* = 5.5 Hz), 4.96 (1 H, m), [minor isomer] 0.07 (3 H, s), 0.09 (3 H, s), 0.89 (9 H, s), 1.23 (3 H, d, *J* = 6.2 Hz), 1.6 (6 H, m), 3.6 (2 H, m), 3.75 (3 H, s), 3.82 (1 H, dq, *J* = 5.1, 6.2 Hz), 4.23 (1 H, d, *J* = 5.1 Hz), 4.9 (1 H, m); IR (film) 2930, 2860, 2240, 1716, 1460, 1435, 1375, 1350, 1242, 1200, 1184, 1120, 1075, 1010, 980, 962, 910, 870, 832, 815, 776, 750. Anal. Calcd for $C_{18}H_{32}O_5Si$: C, 60.64; H, 9.05. Found: C, 60.55; H, 9.00.

(4*R*,5*S*)-Methyl 5-Hydroxy-4-(2′-tetrahydropyranyloxy)-2-hexynoate (7e). A solution of **7d** (1.199 g, 3.36 mmol) in dry THF (50 mL) was stirred with 12 mL of 1 M *n*-Bu_4NF in THF at room temperature for 1 h, diluted with ether, and washed with saturated aqueous NH_4Cl and brine. The dried organic layer was concentrated and chromatographed (silica gel, 50 g; 10:1 → 5:1 hexane–ether) to give colorless oil **7e** (731 mg, 90%) as 3:1 mixture of diastereomers: $[\alpha]^{31}_D$ –101° (*c* 2.25, $CHCl_3$); ^1H NMR ($CDCl_3$–D_2O) [major diastereomer] 1.31 (3 H, d, *J* = 6.6 Hz), 1.6 (6 H, m), 3.6 (2 H, m), 3.78 (3 H, s), 4.02 (1 H, dq, *J* = 3.8, 6.6 Hz), 4.50 (1 H, d, *J* = 3.8 Hz), 4.91 (1 H, m), [minor isomer] 1.28 (3 H, d, *J* = 6.2 Hz), 1.6 (6 H, m), 3.6 (2 H, m), 3.78 (3 H, s), 4.01 (1 H, dq, *J* = 3.5, 6.2 Hz), 4.39 (1 H, d, *J* = 3.5 Hz), 4.88 (1 H, m); IR (film) 3450, 2920, 2880, 2230, 1700, 1435, 1240, 1118, 1065, 1020, 960, 905, 868, 842, 812, 750.

(4*R*,5*S*)-Methyl 5-[(Carbamoyl)oxy]-4-hydroxy-2-hexynoate (7f). Chlorosulfonyl isocyanate (0.070 mL, 0.80 mmol) was added dropwise to a stirred solution of **7e** (121 mg, 0.50 mmol) in dry CH_2Cl_2 (10 mL) at –78 °C under Ar atmosphere, and stirring was continued for 30 min. After 10 mL of water was added, the cold bath was removed, and the mixture was vigorously stirred at room temperature for 5 min and then at 60 °C for 5 h to remove CH_2Cl_2 and to hydrolyze the chlorosulfonyl group. The aqueous solution was saturated with NaCl and extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$ and

NH_4Cl, dried over $MgSO_4$, and concentrated. The residue was chromatographed (silica gel, 7 g; 1:5 CH_2Cl_2–ether) to give 80 mg of crystalline **7f** (79%): mp 110–111 °C (recrystallized from AcOEt–hexane); $[\alpha]^{19}_D$ –56.4° (*c* 2.38, MeOH); ^1H NMR (90 MHz) 1.36 (3 H, d, *J* = 6.7 Hz), 3.31 (1 H, d, *J* = 7.2 Hz), 3.81 (3 H, s), 4.60 (1 H, dd, *J* = 3.2, 7.2 Hz), 4.86 (2 H, br), 5.00 (1 H, dq, *J* = 3.2, 6.7 Hz); IR (KBr) 3450, 3300, 3270, 2230, 1720, 1602, 1432, 1495, 1480, 1335, 1320, 1260, 1138, 1075, 1033, 998, 935, 755. Anal. Calcd for $C_8H_{11}NO_5$: C, 47.76; H, 5.51; N, 6.96. Found: C, 47.56; H, 5.81; N, 6.82.

(4*R*,5*S*)-Methyl 5-[(Carbamoyl)oxy]-4-[(triethylsilyl)oxy]-2-hexynoate (7g). Alcohol **7f** (282 mg, 1.40 mmol) was stirred with imidazole (220 mg, 3.23 mmol) and Et_3SiCl (0.26 mL, 1.55 mmol) in dry DMF (2 mL) at room temperature for 1.5 h and chromatographed directly on silica gel column (15 g; 20:1 → 2:1 hexane–ether) to afford colorless oil **7g** (440 mg, 100%): $[\alpha]^{20}_D$ –47.9° (*c* 1.61, $CHCl_3$); ^1H NMR (90 MHz) 0.48–1.15 (15 H, m), 1.32 (3 H, d, *J* = 6.5 Hz), 3.78 (3 H, s), 4.60 (1 H, d, *J* = 4.0 Hz), 4.87 (1 H, dq, *J* = 4.0, 6.5 Hz), 4.88 (2 H, br); IR (film) 3480, 3370, 3270, 3195, 2950, 2920, 2880, 2340, 1715, 1600, 1456, 1435, 1412, 1385, 1320, 1250, 1155, 1080, 1040, 1005, 972, 955, 890, 810, 750, 730.

(4*R*,5*S*)-Methyl (*E*)-5-[(Carbamoyl)oxy]-4-[(triethylsilyl)oxy]-2-hexenoate (4b). A solution of **7g** (51.5 mg, 0.163 mmol) in MeOH (5 mL) was stirred with 5 mg of 5% Pd on $CaCO_3$ poisoned with lead under H_2 atmosphere (1 atm) at room temperature for 10 min; the reaction was carefully followed by TLC analysis, which indicated the reaction completed within 10 min. The mixture was filtered through Celite, and the concentrated filtrate was chromatographed (silica gel 1 g, 2:1 hexane–ether) to afford **4b** as a colorless oil (50 mg, 97%): $[\alpha]^{18}_D$ +13.7° (*c* 2.89, $CHCl_3$); ^1H NMR (200 MHz) 0.5–0.7 (6 H, m), 0.8–1.1 (9 H, m), 1.23 (3 H, d, *J* = 6.6 Hz), 3.75 (3 H, s) 4.62 (2 H, br), 4.84 (1 H, dq, *J* = 4.4, 6.6 Hz), 5.43 (1 H, ddd, *J* = 1.2, 4.4, 8.5 Hz), 5.87 (1 H, dd, *J* = 1.2, 11.8 Hz), 6.14 (1 H, dd, *J* = 8.5, 11.8 Hz); IR (film) 3470, 3370, 3295, 3195, 2955, 2925, 2880, 1722, 1654, 1601, 1460, 1440, 1410, 1376, 1332, 1235, 1204, 1182, 1146, 1082, 1035, 1005, 820, 750, 730. Anal. Calcd for $C_{14}H_{27}NO_5Si$: C, 52.97; H, 8.57; N, 4.41. Found: C, 53.08; H, 8.51; N, 4.75.

(4*R*,5*R*,6*S*)-5-[(Triethylsilyl)oxy]-4-[(methoxycarbonyl)methyl]-6-methylperhydro-1,3-oxazin-2-one (6). To a stirred suspension of *t*-BuOK (160 mg, 1.43 mmol) in dry THF (35 mL) was added quickly a solution of **4b** (423 mg, 1.33 mmol) in dry THF (15 mL) at 0 °C under Ar atmosphere. After 20 min at 0 °C, 1 mL of saturated aqueous NH_4Cl and 40 mL of AcOEt were added, and the mixture was stirred vigorously at room temperature for 5 min and filtered through Celite. The filtrate was concentrated under reduced pressure to give crude product **6**; its 400-MHz ^1H NMR spectrum did not show any signal derived from the 4*S* epimer. The crude residue was chromatographed on silica gel column (5 g) with 5:1 ether–hexane as eluent to afford pure colorless oil **6** (397 mg, 94%): $[\alpha]^{18}_D$ +35.8° (*c* 1.30, $CHCl_3$); ^1H NMR (400 MHz) 0.67 (6 H, q, *J* = 8.2 Hz), 0.98 (9 H, t, *J* = 8.2 Hz), 1.39 (3 H, d, *J* = 6.6 Hz), 2.37 (1 H, dd, *J* = 10.6, 16.5 Hz), 2.83 (1 H, dd, *J* = 2.5, 16.5 Hz), 3.38 (1 H, t, *J* = 8.5 Hz), 3.58 (1 H, dddd, *J* = 0.4, 2.5, 8.5, 10.6 Hz), 3.74 (3 H, s), 4.16 (1 H, dq, *J* = 8.5, 6.6 Hz), 5.91 (1 H, br); IR (film) 3350, 3260, 3140, 2960, 2925, 2890, 1735, 1720, 1455, 1440, 1412, 1400, 1360, 1330, 1296, 1240, 1200, 1174, 1126, 1078, 1006, 858, 746, 732.

(3*R*,4*R*,5*S*)-3-Benzamido-5-hydroxy-5-hexanolide (15). Carbamate **6** (21 mg, 0.066 mmol) was heated at 60 °C with 0.5 mL of 1 N aqueous NaOH in EtOH (1 mL) for 12 h. The mixture was cooled to 0 °C and small pieces of dry ice were added until the precipitation ceased, followed by the addition of $NaHCO_3$ (30 mg, 0.36 mmol) and a solution of PhCOCl (41 mg, 0.29 mmol) in acetone (0.5 mL). After 12 h at room temperature, concentrated HCl was added until pH of the mixture became ca. 2. Diluted with saturated aqueous NH_4Cl, the mixture was extracted with AcOEt. The organic layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed (silica gel, 2 g; 1:1 hexane–AcOEt) and recrystallized from AcOEt–hexane to give **15** (12 mg, 73%) as colorless needles: mp 152–154 °C; $[\alpha]^{20}_D$ +42° (*c* 0.41, EtOH); ^1H NMR (200 MHz) 1.38 (3 H, d, *J* = 6.6 Hz), 2.63 (1 H, dd, *J* = 4.6, 18.5 Hz), 2.96 (1 H, br d, *J* = 4.2 Hz, OH), 3.17 (1 H, dd, *J* = 9.1, 18.5 Hz), 4.08 (1 H, ddq, *J* = 4.2, 4.9, 6.6 Hz), 4.34 (1 H, dd, *J* = 3.6, 4.9 Hz), 4.88 (1 H, dddd, *J* = 3.6, 4.6, 7.1, 9.1 Hz), 6.93 (1 H, br d, *J* = 7.1 Hz, NH), 7.52 (3 H, m), 7.84 (2 H, m); IR (KBr) 3325, 3050, 3010, 2955, 2920, 2860, 1740, 1720, 1638, 1598, 1575, 1542, 1492, 1455, 1408, 1382, 1370, 1338, 1320, 1284, 1258, 1216, 1187, 1135, 1100, 1086, 1035, 1026, 1004, 964, 922, 850, 692. Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.55; H, 6.28; N, 5.62.

***N*-Benzoylristosamine (2b).** To a stirred solution of **15** (61 mg, 0.24 mmol) in dry THF (10 mL) was added dropwise 1.23 mL of 1 M DIBAL in hexane at –98 °C under Ar atmosphere. After 50 min at the same temperature the reaction was quenched with 1 mL of 5:1 mixture of MeOH–H_2O, and then the cold bath was removed. The mixture was stirred at room temperature for 30 min and filtered through Celite. The filtrate was concentrated and chromatographed on silica gel (5 g) column with 5:1 AcOEt–hexane as eluent to give crystalline **2b** (40 mg, 65%), recrystallized from AcOEt–hexane: mp 132–134 °C; $[\alpha]^{28}_D$ –10° (after 10 min), –24° (after 3 h, constant) (*c* 0.20, EtOH); ^1H NMR (400 MHz, Me_2SO-d_6; 2:1 anomeric mixture of furanose after 1 h) [major anomer] 1.07 (3 H, d, *J* = 6.5 Hz, H6), 1.77 (1 H, ddd, *J* = 2.3, 4.7, 13.4 Hz, H2), 2.31 (1 H, ddd, *J* = 5.3, 9.1, 13.4 Hz, H2), 3.64 (1 H, ddq, *J* = 4.4, 4.9, 6.5 Hz, H5), 3.89 (1 H, dd, *J* = 4.9, 5.3 Hz, H4), 4.40 (1 H, dddd, *J* = 4.7, 5.3, 7.8, 9.1 Hz, H3), 4.69 (1 H, d, *J* = 4.4 Hz, C5-OH), 5.40 (1 H, dt, *J* = 2.3, 5.3, Hz, H1), 6.35 (1 H, d, *J* = 5.3 Hz, Cl-OH), 7.49 (3 H, m), 7.84 (2 H, m), 8.40 (1 H, d, *J* = 7.8 Hz, NH), [minor isomer] 1.09 (3 H, d, *J* = 6.2 Hz, H6), 2.04 (2 H, dd, *J* = 3.7, 7.8 Hz, H2), ~3.68 (1 H, m, H5), 3.68 (1 H, m, H4), 4.57 (1 H, d, *J* = 3.0 Hz, C5-OH), 4.65 (1 H, dq, *J* = 5.3, 7.8 Hz, H3), 5.40 (1 H, m, H1), 6.36 (1 H, d, *J* = 5.3 Hz, C1-OH), 7.49 (3 H, m), 7.84 (2 H, m), 8.56 (1 H, d, *J* = 7.8 Hz, NH); IR (KBr) 3360, 3295, 3075, 2970, 2920, 1635, 1580, 1540, 1492, 1448, 1405, 1320, 1154, 1076, 1062, 1044, 1032, 1020, 995, 935, 918, 876, 860, 820, 802, 700.

Model Studies in the Quassimarin Series: Total Synthesis of De-A-quassimarin

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trans-Decalone **5** has been converted into (±)-de-A-quassimarin (**6**) via a sequence of transformations involving (a) introduction of a latent acetic acid unit into the C(14) position of **13**, (b) construction of the C(8),C(13) epoxymethano ether bridge, (c) elaboration of the trans-diaxial arrangement of hydroxyl groups at C(11) and C(12), and (d) adjustment of the oxidation state at C(7) for eventual δ-lactone formation.

Synthetic studies on quassinoids,[1] bitter principles of simaroubaceous plants, continue to occupy the attention of numerous synthetic organic chemists worldwide.[2] Much of the activity in this area has been due in part to the fact

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