A Simple Strategy for Determining the Absolute Configurations of Acyclic 1,2,4,6,8-Pentols

Yuji Mori,* Tomoko Sawada, Natsue Sasaki, and Hiroshi Furukawa

Contribution from the Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

Received July 17, 1995. Revised Manuscript Received November 20, 1995[⊗]

Abstract: A simple procedure for assigning the absolute stereochemistry of 1,3-polyols containing four chiral centers using the CD exciton chirality method is presented. Eight possible diastereoisomers of 10-undecene-1,2,4,6,8-pentols with established absolute configurations were used as models to develop the strategy. The C2 and C4 configurations are established from the sign and amplitude of the difference CD spectrum between the pentabenzoate and the 1-*O*-pivaloyl tetrabenzoate, respectively, thus reducing the possible configurations from 16 to 4. The stereochemistry of the C8 chiral center is directly assigned from the CD analysis of the 1-*O*-pivaloyl tetrabenzoate; tetrabenzoates having a 2,8-*syn* configuration exhibit weak CD curves whereas the 2,8-*anti* tetrabenzoates exhibit strong exciton split curves. This analysis further reduces the possible stereoisomers to two. The final configurational assignment at C6 is performed by the ^{13}C NMR analysis of the diacetonide derived from the 1-*O*-pivaloyl 2,4,6,8-tetrols. Advantages of the present method are that the requisite transformations involve only four simple steps and that reference samples are not necessary.

Introduction

The 1,3-skipped polyol systems are widely distributed in nature and form the basic structure of clinically valuable polyene macrolide antibiotics. About 40 planar structures of the over 200 known polyene macrolides have been determined,[1] but their stereochemical elucidation remains a serious and challenging problem, and many efforts have been devoted to their solution. The full structures of amphotericin B[2] and roxaticin[3] have been determined by X-ray crystallography, and the stereochemical structures of pimaricin[4] and candidin[5] were assigned by sophisticated NMR analysis. The stereochemistry of mycoticins,[6] nystatin A_1,[7] pentamycin,[8] roflamycoin,[9] and filipin III,[10] as well as the partial stereochemistry of lienomycin,[11] has been identified by a combination of chemical degradation, partial synthesis, and spectroscopy. Most of these studies involve multistep chemical manipulations and invoke a strong impetus for the development of a simple and reliable spectroscopic method in this area.

Stereochemical assignment of acyclic skipped polyols using the CD exciton chirality method[12] has recently emerged. The most comprehensive studies of simple 1,3-diols were accomplished by Harada,[13] and a bichromophoric exciton chirality method was successfully applied to 1,2,4,6-tetrols by Nakanishi.[14] We have reported the first attempt at using a difference CD (DIF CD) method to assign the absolute configurations of 1,3-polyols in a reiterative manner.[15] Oishi has also reported another reiterative procedure.[16] The DIF CD method originally developed for 1,3-polyols having a terminal allylic system[15,17] has proven its potential applicability to acyclic systems with a high degree of conformational complexity. Dehydration of the terminal primary alcohol of 1,3-polyols yields an olefinic group which can give an exciton-type interaction with benzoates at the secondary alcohol centers. The sign of the CD band due to the coupling of the subterminal benzoate, which is characteristic of the chirality at that center, is extracted from the CD spectrum by taking the difference CD curve with that of the polyol benzoylated only at the secondary centers. The DIF CD method has further proven to be extendable to 1,2,4-triol systems for assigning the configuration at the C2 chiral center by extracting the terminal 1,2-dibenzoate exciton interaction.[18] Extension of the same principle to 1,2,4,...,*n*-polyols would be very important because such polyol systems are typically derived from various natural products by either periodate or ozonolysis degradation, as was the case for lienomycin.[11] We demonstrate here a new

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) Omura, S.; Tanaka, H. In *Macrolide Antibiotics: Chemistry, Biology and Practice;* Omura, S., Ed.; Academic Press: New York, 1984; pp 351−401.

(2) (a) Ganis, P.; Avitabile, G.; Mechlinski, W.; Schaffner, C. P. *J. Am. Chem. Soc.* **1971**, *93*, 4560−4564. (b) Mechlinski, W.; Schaffner, C. P.; Ganis, P.; Avitable, G. *Tetrahedron Lett.* **1970**, 3873−3876.

(3) Maehr, H.; Yang, R.; Hong, L.-N.; Liu, C.-M.; Hatada, M. H.; Todaro, L. J. *J. Org. Chem.* **1989**, *54*, 3816−3819.

(4) Lancelin, J.-M.; Beau, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 4060−4061.

(5) Pawlak, J.; Sowinski, P.; Borowski, E.; Gariboldi, P. *J. Antibiot.* **1993**, *46*, 1598−1604.

(6) (a) Schreiber, S. L.; Goulet, M. T.; Sammakia, T. *Tetrahedron Lett.* **1987**, *28*, 6005−6008. (b) Schreiber, S. L.; Goulet, M. T. *Tetrahedron Lett.* **1987**, *28*, 6001−6004. (c) Schreiber, S. L.; Goulet, M. T.; Schulte, G. *J. Am. Chem. Soc.* **1987**, *109*, 4718−4720. (d) Schreiber, S. L.; Goulet, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 8120−8122.

(7) (a) Lancelin, J.-M.; Beau, J.-M. *Tetrahedron Lett.* **1989**, *30*, 4521−4524. (b) Prandi, J.; Beau, J.-M. *Tetrahedron Lett.* **1989**, *30*, 4517−4520. (c) Nicolaou, K. C.; Ahn, K. H. *Tetrahedron Lett.* **1989**, *30*, 1217−1220.

(8) Oishi, T. *Pure Appl. Chem.* **1989**, *61*, 427−430.

(9) (a) Rychnovsky, S. D.; Griesgraber, G.; Schlegel, R. *J. Am. Chem. Soc.* **1994**, *116*, 2623−2624. (b) Rychnovsky, S. D.; Griesgraber, G.; Schlegel, R. *J. Am. Chem. Soc.* **1995**, *117*, 197−210.

(10) Rychnovsky, S. D.; Richardson, T. I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1227−1230.

(11) Pawlak, J.; Nakanishi, K.; Iwashita, T.; Borowski, E. *J. Org. Chem.* **1987**, *52*, 2896−2901.

(12) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry;* University Science Books: Mill Valley, CA, 1983.

(13) Harada, N.; Saito, A.; Ono, H.; Gawronski, J.; Gawronska, K.; Sugioka, T.; Uda, H.; Kuriki, T. *J. Am. Chem. Soc.* **1991**, *113*, 3842−3850.

(14) Zhou, P.; Zhao, N.; Rele, D. N.; Berova, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1993**, *115*, 9313−9314.

(15) Mori, Y.; Kohchi, Y.; Suzuki, M.; Furukawa, H. *J. Am. Chem. Soc.* **1992**, *114*, 3557−3559.

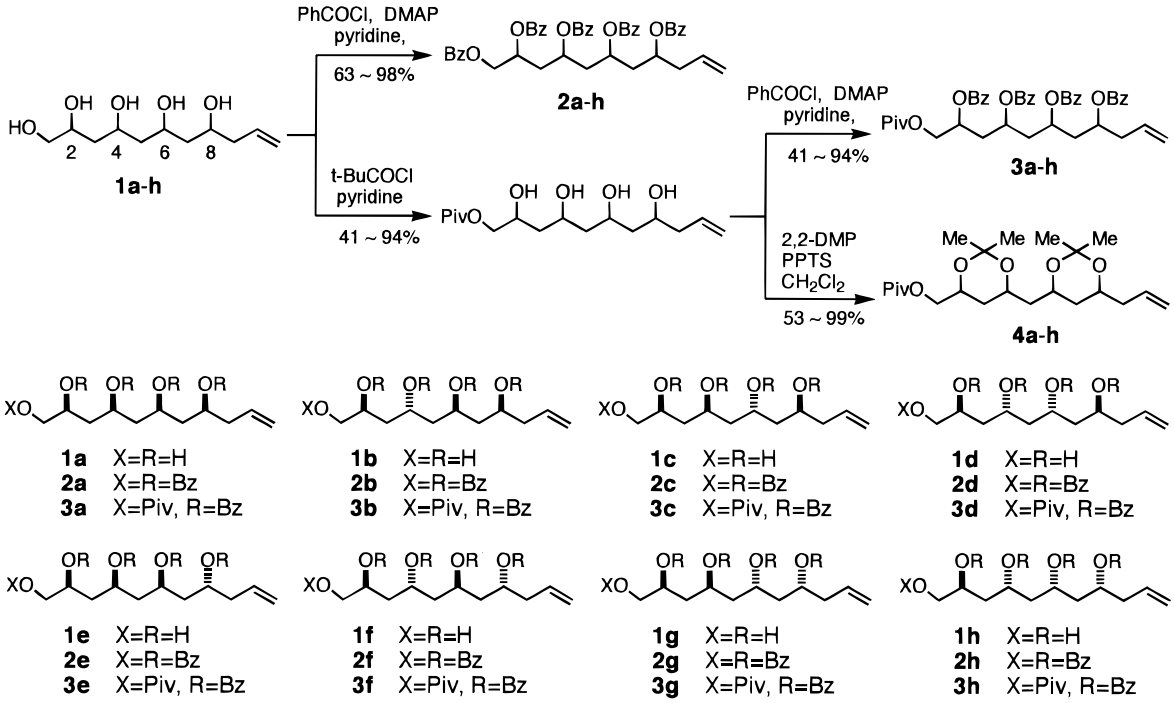
(16) Nakata, T.; Noriaki, H.; Nakashima, K.; Oishi, T. *Chem. Pharm. Bull.* **1987**, *35*, 4355−4358.

(17) Mori, Y.; Kohchi, Y.; Suzuki, M.; Furukawa, H. *Chem. Pharm. Bull.* **1992**, *40*, 1934−1936.

(18) Mori, Y.; Furukawa, H. *Tetrahedron,* **1995**, *51*, 6725−6738.

0002-7863/96/1518-1651$12.00/0

Scheme 1



strategy for determining the absolute configurations of 1,2,4,6,8-pentols having four chiral centers by employing a combination of the DIF CD and ^{13}C NMR analyses. This paper describes the strategic principle using model pentols with established structures.

Results and Discussion

Derivatizations of Pentol Derivatives and the Definition of the Absolute Configuration. One enantiomeric series of 10-undecene-1,2,4,6,8-pentols was synthesized based on the four-carbon chain extension approach.[19] The stereochemistry of C2 was fixed as the β (*S*)-configuration and the eight possible diastereoisomeric pentols **1a**−**h** with established absolute configurations were used as models to develop the strategy. Pentols **1a**−**h** were transformed into pentabenzoates **2a**−**h**, respectively, by reaction with benzoyl chloride−pyridine and the 1-*O*-pivaloyl-tetrol derivatives obtained by selective protection of **1a**−**h** with pivaloyl chloride in pyridine were converted into the corresponding tetrabenzoates **3a**−**h** by benzoylation and acetonides **4a**−**h** by treatment with 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid in dichloromethane (Scheme 1).

The definition of the absolute configuration using the *R* and *S* nomenclature is universal and has been extensively used. However, the *R* and *S* designations may vary with substituents and are sometimes inconvenient to express the absolute configuration of a group of acyclic polyols with multiple chiral centers. Therefore, an alternative of α and β rather than *R* and *S* designations to express absolute configuration is used for convenience, as well as the *syn* and *anti* nomenclature of expressing relative configuration, where the polyol chain is depicted as an extended zigzag form in a single plane.

Absolute Configurations at C2 and C4 Positions. The absolute configuration at C2 was first determined. The CD spectra of **2a**−**h** (Figure 1a) and **3a**−**h** (Figure 1b) reflect the overall interactions of the exciton chiralities between all benzoate chromophores. Subtraction of the CD curve of **2** from that of **3** gives a DIF CD curve mainly attributable to the terminal 1,2-dibenzoate exciton coupling because of cancellation of the exciton interactions between the secondary benzoate chromophores at the C2, -4, -6, and -8 positions (Scheme 2). A positive or negative first Cotton effect at 236 nm is diagnostic for the 2β- or 2α-configuration, respectively,[18] which is independent of the configurations at the remaining chiral centers. The DIF CD spectra of the eight stereoisomers clearly exhibited a positive DIF CD Cotton effect due to the 1,2-exciton coupling, which is correlated with a β-configuration at C2 (Figure 1c).

Inspection of the amplitude of the DIF CD spectra provided important stereochemical information on the C4 chiral center; the 2,4-*syn* benzoates showed a value of $|A| > 9$ (Table 1, entries 1, 3, 5, and 7), while the benzoates having a 2,4-*anti* relationship showed $|A| < 8$ (Table 1, entries 2, 4, 6, and 8). The difference in amplitude, $|A| > 9$ vs $|A| < 8$, can be rationalized by considering the remote 1,4-dibenzoate exciton interaction. Thus, 2,4-*syn* benzoates have strong positive 1,2- and weak positive 1,4-interactions, hence the amplitudes are larger, whereas a weak 1,4-interaction of the 2,4-*anti* benzoates is opposite to the interaction arising from the 1,2-benzoyl groups and therefore amplitudes are diminished (Figure 2). The same trend was also observed in the DIF CD spectra of one enantiomeric series of 1,2,4,6-tetrol derivatives with three chiral centers; the 2,4-*syn* isomers have a value larger ($|A| = 10.0-10.9$) than the 2,4-*anti* isomers ($|A| = 6.0-7.7$). Thus, the sign and magnitude of the DIF CD spectrum allow one to determine the absolute configurations at C2 and C4, respectively, and the number of unknown stereoisomers of a 1,2,4,6,8-pentol decreases from sixteen to four.

Absolute Configuration at the C8 Position. The perbenzoylated derivatives **2a**−**h** exhibited distinctive and predictable CD spectra (Figure 1a). All 2,8-*syn* isomers (**2a**−**d**) exhibited a positive Cotton effect while all 2,8-*anti* isomers (**2e**−**h**) showed a strong negative effect. These differences are diagnostic for the assignment of the relative stereochemistry of the

(19) (a) Mori, Y.; Suzuki, M. *Tetrahedron Lett.* **1989**, *30*, 4387−4388. (b) Mori, Y.; Suzuki, M. *Tetrahedron Lett.* **1989**, *30*, 4383−4386. (c) Mori, Y.; Takeuchi, A.; Kageyama, H.; Suzuki, M. *Tetrahedron Lett.* **1988**, *29*, 5423−5426. (d) Mori, Y.; Asai, M.; Furukawa, H. *Heterocycles* **1992**, *34*, 1281−1284.

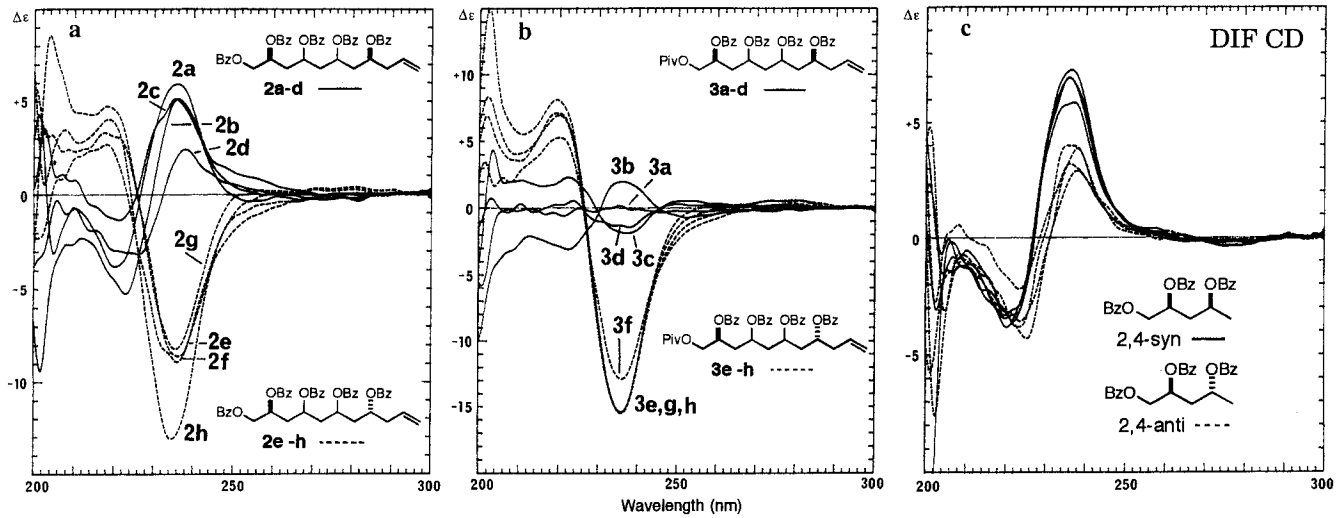


Figure 1. CD spectra of derivatized pentols in methanol: (a) CD of **2a**−**h**; (b) CD of **3a**−**h**; (c) DIF CD between **2a**−**h** and **3a**−**h**.

Scheme 2

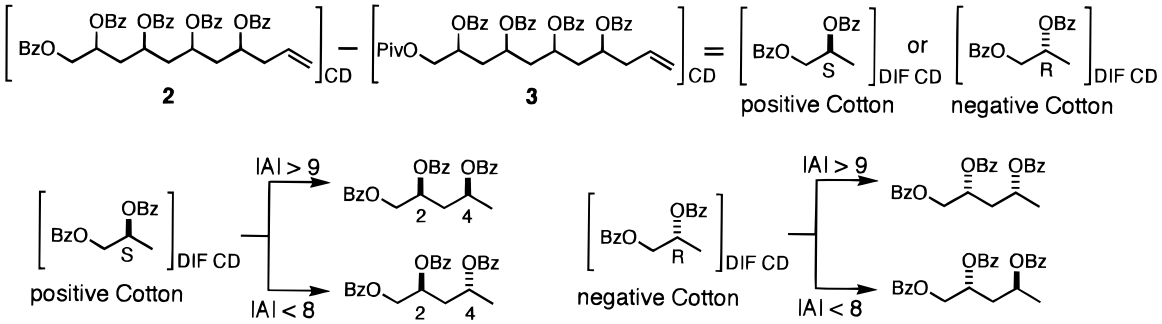


Table 1. CD Data of Compounds **2** and **3** and their DIF CD Data

	pentabenzoate **2**		tetrabenzoate **3**			DIF CD		configuration
entry no.	compd no.	nm ($\Delta\epsilon$)	compd no.	nm ($\Delta\epsilon$)	*A*	nm ($\Delta\epsilon$)	*A*	C2,4,6, and 8
1	**2a**	235.8 (+6.0) 220.2 (−3.8)	**3a**	no Cotton	0	236.8 (+5.9) 219.6 (−3.3)	+9.2	*ββββ*
2	**2b**	236.0 (+5.2) 223.0 (−5.3)	**3b**	236.2 (+2.0) 222.4 (−3.1)	+5.1	236.0 (+3.2) 223.4 (−2.2)	+5.4	*βαββ*
3	**2c**	235.4 (+5.2) 221.4 (−1.3)	**3c**	237.2 (−1.9) 222.4 (+2.3)	−4.2	235.8 (+6.9) 221.8 (−3.6)	+10.5	*ββαβ*
4	**2d**	237.8 (+2.4) 226.2 (−3.1)	**3d**	238.0 (−1.4) 223.6 (+0.5)	−1.9	237.8 (+3.9) 223.6 (−3.6)	+7.5	*βααβ*
5	**2e**	236.4 (−8.6) 217.6 (+3.3)	**3e**	236.0 (−15.5) 220.0 (+6.9)	−22.4	235.8 (+6.9) 220.2 (−3.8)	+10.7	*βββα*
6	**2f**	236.2 (−8.9) 218.2 (+2.7)	**3f**	236.0 (−12.9) 220.2 (+5.3)	−18.2	235.4 (+4.0) 223.2 (−3.8)	+7.8	*βαβα*
7	**2g**	235.6 (−8.2) 218.4 (+4.7)	**3g**	235.8 (−15.5) 219.4 (+8.1)	−23.6	236.2 (+7.3) 219.8 (−3.4)	+10.7	*ββαα*
8	**2h**	234.6 (−13.1) 218 (+4.1)	**3h**	235.8 (−15.4) 219.6 (+7.1)	−22.5	237.8 (+2.9) 225.4 (−4.3)	+7.2	*βααα*

Figure 2. The exciton couplings of the benzoate at C1 to benzoates at the C2 position (solid arrow) and the C4 position (dotted arrow).

C2 and C8 positions, but the sign of the Cotton effects observed, of course, reflects the net chirality of all the possible benzoate-benzoate interactions including the 1,2-dibenzoate interaction. We then turned our attention to the CD spectra of **3a**−**h** (Figure 1b). These spectra are also characterized by two different shapes; tetrabenzoates having a 2,8-*syn* relationship exhibited weak CD Cotton curves (**3a**−**d**, $|A| = 0-5.1$) and the 2,8-*anti* tetrabenzoates exhibited strong exciton split curves (**3e**−**h**, $|A| = 18.2-23.6$) (Table 1). These trends are generally observed for the perbenzoates of 1-*O*-pivaloyl 1,2,4,...,*n*-polyols (n = even number) with up to four chiral centers so far.[20] All 2,*n*-*anti* isomers gave rise to a strong coupling with $|A|$ values >18, whereas for the 2,*n*-*syn* isomers, weak couplings were observed and the values are $|A| < 6$.

The most preferred conformation of acyclic 1,3-dibenzoates adopts an extended zigzag form, and two benzoates of a *syn* isomer are aligned parallel while the angle between the two benzoates of an *anti* isomer is ca. 120° as described by Harada.[13]

(20) The 1-*O*-anthroyl 2,4,6-tricinnamate derivatives of heptane-1,2,4,6-tetrols show similar characteristic CD spectra. See ref 14.

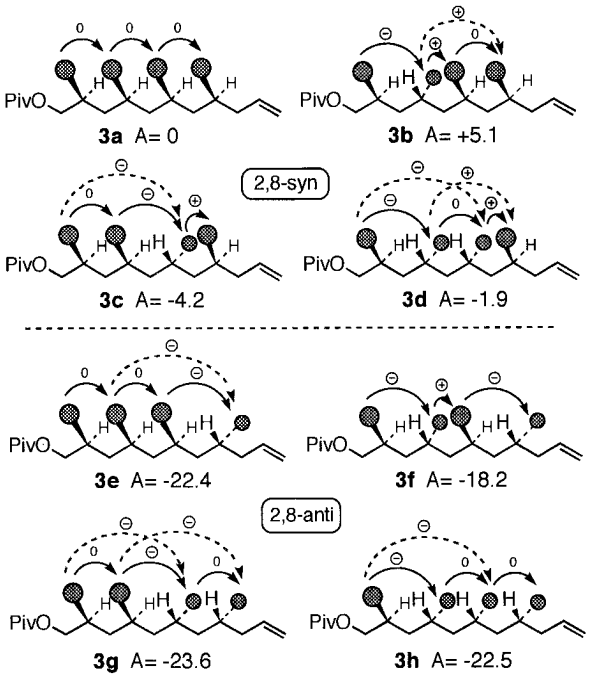
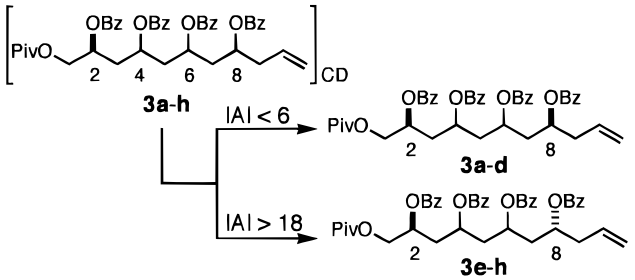


Figure 3. The exciton couplings of **3a**−**h**. The solid and dotted arrows indicate 1,3- and 1,5-interactions, respectively.

Scheme 3



Hence, the *syn* isomer shows a negligible exciton coupling and the *anti* isomer produces a strong positive or negative coupling depending on its chirality. The differences in the intensities and signs of the Cotton effects are rationally explained by considering the additive effects of each 1,3- and 1,5-pairwise interaction (Figure 3). In all 2,8-*syn* cases the amplitudes are small because in the four possible C4/C6 permutations, the arrangements are all *syn* or otherwise contain two *anti* arrangements and hence the coupling in this region is small or nil. The small coupling of **3b**, **3c**, and **3d** is attributed to 1,5-remote exciton interactions. In contrast, all 2,8-*anti* isomers have one *anti*-interacting benzoate pair and hence the coupling is intense (Figure 2). The *A* values of **3e**, **3g**, and **3h** are slightly stronger than that of **3f** by the additional exciton coupling caused by the weak negative 1,5-remote interactions. Therefore, the net chirality is ultimately correlated with the chirality between the C2 and C8 positions: the 2β− and 8β-configurations were assigned for **3a**−**d** based on the weak CD amplitudes, whereas the strong negative Cotton effects observed for **3e**−**h** indicate that the C2 and C8 benzoates have a negative chirality, namely, 2β− and 8α-configurations (Scheme 3).

Absolute Configuration at the C6 Position. The remaining unknown stereocenter at C6 was determined by the ^{13}C NMR acetonide analysis developed by Rychnovsky.[21] In general, it has been observed that 1,3-*syn*-diol acetonides have acetal methyl shifts at 19 and 30 ppm, while 1,3-*anti*-diol acetonides have methyl shifts at about 25 ppm. This analysis was used to determine the relative configuration of **4a**−**h**. The ^{13}C NMR analysis data are summarized in Table 2. The data were consistent with the above generalizations and allowed us to assign the relative configurations of C2/C4 and C6/C8.[22] The absolute configuration at C6 can be determined in a straightforward manner because the configurations at C2, C4, and C8 have already been assigned.

Table 2. ^{13}C Chemical Shifts of the Acetonide Methyls of **4a**−**h**

compd	acetonide methyl chemical shift (ppm)				configuration C2/4, C6/8
4a	19.70	19.76	30.03	30.19	*syn*, *syn*
4b	19.80	24.44	24.50	30.24	*anti*, *syn*
4c	19.69	24.60	24.62	30.06	*syn*, *anti*
4d[a]	24.59	24.62	24.74	24.85	*anti*, *anti*
4e	19.69	24.78	24.90	30.03	*syn*, *anti*
4f	24.59	24.70	24.90	27.14	*anti*, *anti*
4g	19.75	19.87	30.10	30.28	*syn*, *syn*
4h	19.78	24.63	24.69	30.20	*anti*, *syn*

[a] Isolated in 5% yield. The 4,6-monoacetonide (δ_C of acetonide methyls; 19.67 and 30.19 ppm) was obtained in 74% yield.

Conclusion

We have developed a unique and simple method for determining the absolute configurations of conformationally flexible acyclic 1,3-polyols with a terminal 1,2-diol group. The DIF CD and CD analyses directly provided the stereochemical information at the C2, C4, and C8 positions. It is worthwhile to emphasize that direct assignment of the relative and/or absolute configurations of the most remote C2 and C8 chiral centers is the first example and makes the present method useful.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on JEOL Alpha-400 and -600 spectrometers. IR spectra were measured on a JASCO IR-800 spectrometer. Mass spectra were obtained with a JEOL HX-110 spectrometer. Optical rotations were determined on a JASCO DIP-370 digital polarimeter. UV measurements were performed on a JASCO UVIDEC-610C spectrophotometer using methanol as a solvent. CD spectra were recorded in methanol (1-cm quartz cell) using a JASCO J-600 spectropolarimeter driven by a JASCO DP-600 data processor. Prior to UV and CD measurements, all samples were purified by normal-phase HPLC (5 μm silica gel). The concentrations of methanol solutions were determined on the basis of the experimentally determined average benzoate UV ϵ's at 229 nm (tetrabenzoate, ϵ 48 000; pentabenzoate, ϵ 59 500).

Preparation of 1a−**h.** A typical procedure is as follows. Pentol **1** (5.0 mg, 0.04 mmol) was dissolved in pyridine (0.5 mL) and benzoyl chloride (46 μL, 0.4 mmol) and 4-(dimethylamino)pyridine (0.5 mg) were added. The reaction mixture was stirred at room temperature for 15 h and then treated with methanol (0.1 mL). After removal of the solvents *in vacuo*, the residue was purified by flash chromatography (30% ethyl acetate/hexane) to give pentabenzoate **2**: **2a** (87%), **2b** (83%), **2c** (63%), **2d** (85%), **2e** (98%), **2f** (97%), **2g** (84%), and **2h** (82%).

(2*S*,4*S*,6*S*,8*S*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2a): $[\alpha]^{25}_D$ +5.21° (*c* 0.33, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1460, 1275, 1115 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (1H, m), 2.23 (3H, m), 2.38 (4H, m), 4.40 (1H, dd, J = 12.0, 5.9 Hz), 4.51 (1H, dd, J = 12.0, 3.7 Hz), 4.96 (1H, d, J = 10.0 Hz), 4.99 (1H, d, J = 17.1 Hz), 5.31 (1H, m), 5.44 (1H, m), 5.50 (1H, m), 5.61 (1H, m), 5.70 (1H, dddd, J = 17.1, 10.0, 7.3, 7.3 Hz), 7.26−7.52 (15H, m),

(21) (a) Rychnovsky, S. D.; Skalitzky, D. J. *Tetrahedron Lett.* **1990**, *31*, 945−948. (b) Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511-3515. (c) Rychnovsky, S. D.; Yang, G.; Powers, J. R. *J. Org. Chem.* **1993**, *58*, 5251−5255.

(22) Compound **4d** was obtained as a minor product (5%). The major product was the 4,6-monoacetonide derivative (74%).

7.91−7.95 (10H, m). HRMS (FAB) *m/z* 755.2850 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*R*,6*S*,8*S*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2b): $[\alpha]^{25}_D$ −3.11° (*c* 0.86, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1465, 1275, 1110 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (1H, m), 2.30−2.42 (5H, m), 2.46 (2H, t, J = 6.6 Hz), 4.40 (1H, dd, J = 12.0, 6.1 Hz), 4.55 (1H, dd, J = 12.0, 3.9 Hz), 5.02 (1H, d, J = 10.3 Hz), 5.07 (1H, d, J = 17.3 Hz), 5.32 (1H, m), 5.43 (2H, m), 5.59 (1H, m), 5.76 (1H, dddd, J = 17.3, 10.3, 7.1, 7.1 Hz), 7.10−7.56 (15H, m), 7.73−7.99 (10H, m). HRMS (FAB) *m/z* 755.2854 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*S*,6*R*,8*S*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2c): $[\alpha]^{25}_D$ +6.96° (*c* 0.45, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1270, 1110 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 2.15 (2H, m), 2.18−2.29 (2H, m), 2.33 (1H, m), 2.42 (1H, m), 2.44 (2H, t, J = 7.3 Hz), 4.45 (1H, dd, J = 12.1, 6.2 Hz), 4.57 (1H, dd, J = 12.1, 3.7 Hz), 5.03 (1H, d, J = 10.3 Hz), 5.05 (1H, d, J = 17.2 Hz), 5.28 (1H, m), 5.40 (1H, m), 5.46 (1H, m), 5.63 (1H, m), 5.74 (1H, dddd, J = 17.2, 10.3, 7.3, 7.3 Hz), 7.12−7.53 (15H, m), 7.74−7.97 (10H, m). HRMS (FAB) *m/z* 755.2851 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*R*,6*R*,8*S*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2d): $[\alpha]^{25}_D$ −1.50° (*c* 1.0, $CHCl_3$). IR ($CHCl_3$) 1720, 1605, 1460, 1280, 1120 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (2H, m), 2.21 (2H, m), 2.45 (4H, m), 4.42 (1H, dd, J = 12.0, 6.1 Hz), 4.56 (1H, dd, J = 12.0, 3.7 Hz), 5.01 (1H, d, J = 10.0 Hz), 5.05 (1H, d, J = 17.1 Hz), 5.28 (1H, m), 5.48 (2H, m), 5.60 (1H, m), 5.75 (1H, dddd, J = 17.1, 10.0, 7.1, 7.1 Hz), 7.22−7.53 (15H, m), 7.84−7.98 (10H, m). HRMS (FAB) *m/z* 755.2849 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*S*,6*S*,8*R*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2e): $[\alpha]^{25}_D$ −39.4° (*c* 1.0, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1270, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.04−2.30 (4H, m), 2.40 (4H, m), 4.47 (1H, dd, J = 12.0, 5.9 Hz), 4.56 (1H, dd, J = 12.0, 3.7 Hz), 4.99 (1H, d, J = 10.3 Hz), 5.00 (1H, d, J = 17.1 Hz), 5.26 (1H, m), 5.43 (1H, m), 5.50 (1H, m), 5.64 (1H, m), 5.72 (1H, dddd, J = 17.1, 10.3, 7.1, 7.1 Hz), 7.19−7.53 (15H, m), 7.81−7.98 (10H, m). HRMS (FAB) *m/z* 755.2855 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*R*,6*S*,8*R*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2f): $[\alpha]^{25}_D$ −37.3° (*c* 0.5, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1270, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (2H, m), 2.23−2.40 (4H, m), 2.46 (2H, t, J = 6.6 Hz), 4.44 (1H, dd, J = 12.1, 6.2 Hz), 4.57 (1H, dd, J = 12.1, 3.7 Hz), 5.03 (1H, d, J = 10.3 Hz), 5.07 (1H, d, J = 17.2 Hz), 5.30 (1H, m), 5.42 (1H, m), 5.46 (1H, m), 5.61 (1H, m), 5.76 (1H, dddd, J = 17.2, 10.3, 7.3, 7.3 Hz), 7.17−7.54 (15H, m), 7.79−7.98 (10H, m). HRMS (FAB) *m/z* 755.2852 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*S*,6*R*,8*R*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2g): $[\alpha]^{25}_D$ −32.0° (*c* 1.25, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1270, 1115 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 2.02 (1H, m), 2.19 (1H, m), 2.26−2.37 (3H, m), 2.43 (1H, m), 2.47 (2H, t, J = 7.0 Hz), 4.48 (1H, dd, J = 11.7, 6.2 Hz), 4.57 (1H, dd, J = 11.7, 3.7 Hz), 5.05 (1H, d, J = 10.0 Hz), 5.07 (1H, d, J = 16.9 Hz), 5.32 (1H, m), 5.40 (1H, m), 5.46 (1H, m), 5.64 (1H, m), 5.77 (1H, dddd, J = 16.9, 10.0, 7.3, 7.3 Hz), 7.12−7.54 (15H, m), 7.77−7.98 (10H, m). HRMS (FAB) *m/z* 755.2850 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

(2*S*,4*R*,6*R*,8*R*)-1,2,4,6,8-Penta-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (2h): $[\alpha]^{25}_D$ −48.0° (*c* 1.2, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1450, 1270, 1110 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 2.07 (1H, m), 2.14−2.30 (3H, m), 2.35−2.46 (4H, m), 4.39 (1H, dd, J = 12.1, 5.9 Hz), 4.51 (1H, dd, J = 12.1, 3.7 Hz), 5.00 (1H, d, J = 9.9 Hz), 5.03 (1H, d, J = 17.2 Hz), 5.33 (1H, m), 5.45 (2H, m), 5.59 (1H, m), 5.74 (1H, dddd, J = 17.2, 9.9, 7.3, 7.3 Hz), 7.20−7.54 (15H, m), 7.82−7.96 (10H, m). HRMS (FAB) *m/z* 755.2849 (M + H), calcd for $C_{46}H_{43}O_{10}$ 755.2853.

Preparation of 3a−h and 4a−h. A typical procedure is as follows. Pentol **1** (14.3 mg, 0.06 mmol) was dissolved in pyridine (0.4 mL) and pivaloyl chloride (22 μL, 0.18 mmol) was added at 0 °C. The reaction mixture was stirred for 30 min and then methanol (50 μL) was added. After 30 min, the mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (2−10% methanol/ethyl acetate) to give the 1-*O*-pivaloyl derivative in 41−94% yield.

The 1-*O*-pivaloyl derivative (5.3 mg, 0.017 mmol) was dissolved in pyridine (0.5 mL) and benzoyl chloride (30 μL, 0.255 mmol) and 4-(dimethylamino)pyridine (0.5 mg) were added. The reaction mixture was stirred at room temperature for 12−24 h. After addition of methanol (50 μL), the mixture was stirred for 30 min and then extracted with ethyl acetate. The extract was washed with saturated aqueous $NaHCO_3$, water, and brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (15−20% ethyl acetate/hexane) gave **3**: **3a** (99%), **3b** (79%), **3c** (62%), **3d** (87%), **3e** (100%), **3f** (85%), **3g** (89%), and **3h** (70%).

The 1-*O*-pivaloyl derivative (5.2 mg, 0.016 mmol) was dissolved in CH_2Cl_2 (0.5 mL), and 2,2-dimethoxypropane (50 μL) and pyridinium *p*-toluenesulfonate (0.5 mg) were added. The reaction mixture was stirred at room temperature for 1−18 h. After addition of triethylamine (50 μL), the mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (10% ethyl acetate/hexane) to give **4**: **4a** (75%), **4b** (81%), **4c** (85%), **4d** (5%), **4e** (77%), **4f** (85%), **4g** (99%), and **4h** (53%).

(2*S*,4*S*,6*S*,8*S*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3a): $[\alpha]^{25}_D$ +4.17° (*c* 1.0, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1270, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (9H, s), 2.00−2.39 (8H, m), 4.16 (1H, dd, J = 12.0, 6.4 Hz), 4.27 (1H, dd, J = 12.0, 3.7 Hz), 4.96 (1H, d, J = 10.0 Hz), 4.99 (1H, d, J = 17.1 Hz), 5.29 (1H, m), 5.42 (2H, m), 5.48 (1H, m), 5.70 (1H, dddd, J = 17.1, 10.0, 7.1, 7.1 Hz), 7.29−7.52 (12H, m), 7.89−7.95 (8H, m). HRMS (FAB) *m/z* 735.3162 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*R*,6*S*,8*S*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3b): $[\alpha]^{25}_D$ +1.94° (*c* 0.61, $CHCl_3$). IR ($CHCl_3$) 1720, 1605, 1455, 1275, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (9H, s), 2.02 (1H, m), 2.12−2.38 (5H, m), 2.46 (2H, t, J = 6.9 Hz), 4.17 (1H, dd, J = 11.7, 6.4 Hz), 4.29 (1H, dd, J = 11.7, 3.7 Hz), 5.03 (1H, d, J = 10.0 Hz), 5.06 (1H, d, J = 17.5 Hz), 5.30 (1H, m), 5.38 (2H, m), 5.47 (1H, m), 5.76 (1H, dddd, J = 17.5, 10.0, 6.8, 6.8 Hz), 7.11−7.51 (12H, m), 7.73−7.97 (8H, m). HRMS (FAB) *m/z* 735.3165 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*S*,6*R*,8*S*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3c): $[\alpha]^{25}_D$ +6.51° (*c* 0.63, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1275, 1115 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.14 (9H, s), 2.08 (1H, m), 2.14 (2H, m), 2.22 (1H, m), 2.32 (2H, m), 2.44 (2H, t, J = 6.6 Hz), 4.20 (1H, dd, J = 12.1, 6.2 Hz), 4.32 (1H, dd, J = 12.1, 3.7 Hz), 5.03 (1H, d, J = 10.3 Hz), 5.05 (1H, d, J = 17.2 Hz), 5.26 (1H, m), 5.37 (1H, m), 5.41 (1H, m), 5.51 (1H, m), 5.73 (1H, dddd, J = 17.2, 10.3, 7.0, 7.0 Hz), 7.12−7.52 (12H, m), 7.74−7.95 (8H, m). HRMS (FAB) *m/z* 735.3169 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*R*,6*R*,8*S*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3d): $[\alpha]^{25}_D$ +1.63° (*c* 0.8, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1450, 1275, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (9H, s), 2.10 (3H, m), 2.20 (1H, m), 2.31 (1H, m), 2.42 (1H, m), 2.44 (2H, t, J = 7.3 Hz), 4.18 (1H, dd, J = 12.0, 6.1 Hz), 4.30 (1H, dd, J = 12.0, 3.7 Hz), 5.02 (1H, d, J = 10.0 Hz), 5.05 (1H, d, J = 17.1 Hz), 5.27 (1H, m), 5.38−5.52 (3H, m), 5.74 (1H, dddd, J = 17.1, 10.0, 7.1, 7.1 Hz), 7.24−7.46 (12H, m), 7.83−7.91 (8H, m). HRMS (FAB) *m/z* 735.3167 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*S*,6*S*,8*R*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3e): $[\alpha]^{25}_D$ −41.0° (*c* 0.79, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1275, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (9H, s), 2.03−2.19 (4H, m), 2.28−2.42 (4H, m), 4.21 (1H, dd, J = 12.0, 6.4 Hz), 4.30 (1H, dd, J = 12.0, 3.7 Hz), 5.00 (1H, d, J = 10.3 Hz), 5.01 (1H, d, J = 16.8 Hz), 5.25 (1H, m), 5.42 (2H, m), 5.51 (1H, m), 5.71 (1H, dddd, J = 16.8, 10.3, 7.1, 7.1 Hz), 7.19−7.54 (12H, m), 7.80−7.96 (8H, m). HRMS (FAB) *m/z* 735.3163 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*R*,6*S*,8*R*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3f): $[\alpha]^{25}_D$ −34.1° (*c* 1.0, $CHCl_3$). IR ($CHCl_3$) 1720, 1605, 1455, 1280, 1120 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.09 (9H, s), 2.13−2.19 (3H, m), 2.23−2.30 (3H, m), 2.45 (2H, t, J = 6.6 Hz), 4.20 (1H, dd, J = 11.7, 6.6 Hz), 4.30 (1H, dd, J = 11.7, 3.7 Hz), 5.03 (1H, d, J = 10.3 Hz), 5.06 (1H, d, J = 17.2 Hz), 5.29 (1H, m), 5.39 (2H, m), 5.50 (1H, m), 5.75 (1H, dddd, J = 17.2, 10.3, 7.0, 7.0 Hz), 7.19−7.49 (12H, m), 7.80−7.90 (8H, m). HRMS (FAB) *m/z* 735.3164 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*S*,6*R*,8*R*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3g): $[\alpha]^{25}_D$ −33.9° (*c* 0.87, $CHCl_3$). IR ($CHCl_3$) 1720, 1600, 1455, 1275, 1115 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.12 (9H, s), 2.00 (1H, m), 2.06 (1H, m), 2.24−2.36 (4H, m), 2.47 (2H, t, J = 6.6 Hz), 4.22 (1H, dd, J = 12.1, 6.2 Hz), 4.33 (1H, dd, J = 12.1, 3.3 Hz), 5.05 (1H, d, J = 9.9 Hz), 5.08 (1H, d, J = 17.2 Hz), 5.31 (1H, m), 5.38 (2H, m), 5.52 (1H, m), 5.77 (1H, dddd, J = 17.2, 9.9, 7.3, 7.3 Hz), 7.13−7.52 (12H, m), 7.77−7.98 (8H, m). HRMS (FAB) *m/z* 735.3168 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*R*,6*R*,8*R*)-1-*O*-Pivaloyl-2,4,6,8-tetra-*O*-benzoyl-10-undecene-1,2,4,6,8-pentol (3h): $[\alpha]^{25}_D$ −48.0° (*c* 1.2, $CHCl_3$). IR ($CHCl_3$) 1720, 1605, 1455, 1275, 1115 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.09 (9H, s), 2.06 (2H, m), 2.17 (1H, m), 2.26 (2H, m), 2.38 (1H, m), 2.44 (2H, t, J = 6.6 Hz), 4.14 (1H, dd, J = 12.1, 6.2 Hz), 4.27 (1H, dd, J = 12.1, 4.0 Hz), 5.00 (1H, d, J = 10.9 Hz), 5.03 (1H, d, J = 17.1 Hz), 5.31 (1H, m), 5.40 (2H, m), 5.46 (1H, m), 5.74 (1H, dddd, J = 17.1, 10.9, 7.0, 7.0 Hz), 7.20−7.52 (12H, m), 7.79−7.99 (8H, m). HRMS (FAB) *m/z* 735.3170 (M + H), calcd for $C_{44}H_{47}O_{10}$ 735.3166.

(2*S*,4*S*,6*S*,8*S*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4a): $[\alpha]^{25}_D$ +4.4° (*c* 0.78, $CHCl_3$). IR ($CHCl_3$) 1725, 1380, 1165 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.16−1.28 (2H, m), 1.21 (9H, s), 1.38 (6H, s), 1.43 (6H, s), 1.44−1.54 (3H, m), 1.82 (1H, ddd, J = 13.7, 7.3, 7.3 Hz), 2.15 (1H, ddd, J = 13.9, 7.3, 7.3 Hz), 2.30 (1H, ddd, J = 13.9, 6.4, 6.4 Hz), 3.84 (1H, m), 3.96−4.12 (5H, m), 5.05 (1H, d, J = 10.0 Hz), 5.10 (1H, J = 16.8 Hz), 5.81 (1H, dddd, J = 16.8, 10.0, 7.3, 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.70, 19.76, 27.13 (3 × C), 30.03, 30.19, 32.99, 36.19, 38.80, 40.80, 42.58, 64.92, 65.11, 66.74, 67.28, 68.56, 98.44, 98.59, 117.05, 134.14, 178.31. HRMS (FAB) *m/z* 399.2741 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*R*,6*S*,8*S*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4b): $[\alpha]^{25}_D$ +4.84° (*c* 0.42, $CHCl_3$). IR ($CHCl_3$) 1725, 1380, 1165 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (1H, m), 1.20 (9H, s), 1.33 (6H, s), 1.38 (3H, s), 1.42 (3H, s), 1.44−1.65 (5H, m), 2.16 (1H, ddd, J = 14.4, 6.8, 6.8 Hz), 2.30 (1H, ddd, J = 14.4, 6.3, 6.3 Hz), 3.88 (1H, m), 3.97−4.14 (5H, m), 5.04 (1H, d, J = 10.2 Hz), 5.08 (1H, d, J = 17.1 Hz), 5.79 (1H, dddd, J = 17.1, 10.2, 7.1, 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.80, 24.44, 24.50, 27.14 (3 × C), 30.24, 34.66, 36.81, 38.78, 40.79, 42.21, 62.26, 64.93, 65.25, 65.98, 68.75, 98.54, 100.54, 117.01, 134.18, 178.34. HRMS (FAB) *m/z* 399.2746 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*S*,6*R*,8*S*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4c): $[\alpha]^{25}_D$ +10.3° (*c* 0.43, $CHCl_3$). IR ($CHCl_3$) 1725, 1385, 1170 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.20 (9H, s), 1.22 (1H, m), 1.33 (3H, s), 1.34 (3H, s), 1.38 (3H, s), 1.42 (3H, s), 1.46 (1H, m), 1.50−1.64 (4H, m), 2.20 (1H, ddd, J = 14.3, 6.6, 6.6 Hz), 2.31 (1H, ddd, J = 14.3, 7.3, 7.3 Hz), 3.85 (1H, m), 4.00−4.10 (5H, m), 5.05 (1H, d, J = 10.2 Hz), 5.09 (1H, d, J = 16.9 Hz), 5.79 (1H, dddd, J = 16.9, 10.2, 7.3, 7.3 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.69, 24.60, 24.62, 27.14 (3 × C), 30.06, 33.81, 38.26, 38.80, 40.14, 42.20, 62.25, 64.70, 66.33, 66.71, 67.44, 98.72, 100.40, 116.83, 134.46, 178.29. HRMS (FAB) *m/z* 399.2742 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*R*,6*R*,8*S*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4d): $[\alpha]^{25}_D$ +1.32° (*c* 0.08, $CHCl_3$). IR ($CHCl_3$) 1725, 1380, 1170 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.21 (9H, s), 1.34 (12H, s), 1.50−1.68 (5H, m), 1.86 (1H, ddd, J = 13.9, 7.3, 7.3 Hz), 2.20 (1H, ddd, J = 14.3, 6.6, 6.6 Hz), 2.30 (1H, ddd, J = 14.3, 7.0, 7.0 Hz), 3.87 (1H, m), 3.95 (2H, m), 4.01 (1H, m), 4.04 (1H, m), 4.12 (1H, m), 5.05 (1H, d, J = 10.3 Hz), 5.09 (1H, d, J = 17.2 Hz), 5.80 (1H, dddd, J = 17.2, 10.3, 6.6, 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.59, 24.62, 24.74, 24.85, 27.15 (3 × C), 34.21, 37.77, 38.80, 40.14, 41.65, 63.09, 65.05, 65.92, 65.95, 66.10, 100.30, 100.41, 116.92, 134.38, 178.30. HRMS (FAB) *m/z* 399.2747 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*S*,6*S*,8*R*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4e): $[\alpha]^{25}_D$ −13.5° (*c* 0.48, $CHCl_3$). IR ($CHCl_3$) 1725, 1380, 1165 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (9H, s), 1.33 (3H, s), 1.34 (3H, s), 1.38 (3H, s), 1.42 (3H, s), 1.52 (2H, m), 1.61 (3H, m), 1.84 (1H, ddd, J = 13.9, 6.6, 6.6 Hz), 2.20 (1H, ddd, J = 14.2, 6.1, 6.1 Hz), 2.31 (1H, ddd, J = 14.2, 6.8, 6.8 Hz), 3.86 (1H, m), 3.96 (1H, m), 4.00−4.12 (4H, m), 5.06 (1H, d, J = 10.5 Hz), 5.10 (1H, d, J = 17.3 Hz), 5.80 (1H, dddd, J = 17.3, 10.5, 6.6, 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.69, 24.78, 24.90, 27.14 (3 × C), 30.03, 32.98, 37.84, 38.80, 40.12, 42.13, 62.76, 65.31, 66.14, 66.78, 67.29, 98.60, 100.25, 116.89, 134.40, 178.31. HRMS (FAB) *m/z* 399.2741 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*R*,6*S*,8*R*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4f): $[\alpha]^{25}_D$ −30.7° (*c* 0.28, $CHCl_3$). IR ($CHCl_3$) 1725, 1385, 1170 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.20 (9H, s), 1.33 (6H, s), 1.34 (6H, s), 1.50−1.68 (6H, m), 2.19 (1H, ddd, J = 14.3, 7.0, 7.0 Hz), 2.30 (1H, ddd, J = 14.3, 6.6, 6.6 Hz), 3.85 (1H, m), 3.97−4.05 (4H, m), 4.12 (1H, m), 5.04 (1H, d, J = 10.3 Hz), 5.09 (1H, d, J = 16.9 Hz), 5.79 (1H, dddd, J = 16.9, 10.3, 7.0, 7.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.59, 24.70 (2 × C), 24.90, 27.14 (3 × C), 34.66, 38.26, 38.79, 40.14, 41.92, 62.66 (2xC), 65.18, 65.97, 66.25, 100.35, 100.51, 116.82, 134.46, 178.35. HRMS (FAB) *m/z* 399.2739 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*S*,6*R*,8*R*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4g): $[\alpha]^{25}_D$ −17.6° (*c* 0.34, $CHCl_3$). IR ($CHCl_3$) 1725, 1380, 1165 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.10−1.31 (2H, m), 1.20 (9H, s), 1.37 (3H, s), 1.38 (3H, s), 1.41 (3H, s), 1.42 (3H, s), 1.45−1.53 (4H, m), 2.14 (1H, ddd, J = 14.0, 6.6, 6.6 Hz), 2.30 (1H, ddd, J = 14.0, 5.9, 5.9 Hz), 3.88 (1H, m), 4.00−4.12 (5H, m), 5.05 (1H, d, J = 10.3 Hz), 5.08 (1H, d, J = 16.9 Hz), 5.79 (1H, dddd, J = 16.9, 10.3, 7.3, 7.3 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.75, 19.87, 27.15 (3 × C), 30.10, 30.28, 33.84, 36.82, 38.81, 40.78, 43.05, 64.49, 64.70, 66.73, 67.50, 68.83, 98.54, 98.69, 117.03, 134.18, 178.29. HRMS (FAB) *m/z* 399.2745 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

(2*S*,4*R*,6*R*,8*R*)-1-*O*-Pivaloyl-2,4:6,8-di-*O*-isopropylidene-10-undecene-1,2,4,6,8-pentol (4h): $[\alpha]^{25}_D$ −2.93° (*c* 0.17, $CHCl_3$). IR ($CHCl_3$) 1725, 1385, 1165 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 1.20 (1H, m), 1.21 (9H, s), 1.33 (3H, s), 1.34 (3H, s), 1.38 (3H, s), 1.43 (3H, s), 1.52 (2H, m), 1.62 (2H, m), 1.84 (1H, ddd, J = 12.6, 7.3, 7.3 Hz), 2.15 (1H, ddd, J = 13.3, 6.6, 6.6 Hz), 2.30 (1H, ddd, J = 13.3, 6.2, 6.2 Hz), 3.87 (1H, m), 3.95−4.06 (4H, m), 4.12 (1H, m), 5.06 (1H, d, J = 10.3 Hz), 5.09 (1H, d, J = 17.2 Hz), 5.80 (1H, dddd, J = 17.2, 10.3, 7.0, 7.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.77, 24.62, 24.69, 27.15 (3 × C), 29.70, 30.19, 34.22, 36.05, 40.83, 42.05, 62.80, 65.10, 65.51, 65.92, 68.58, 98.47, 100.43, 117.10, 134.13, 178.34. HRMS (FAB) *m/z* 399.2742 (M + H), calcd for $C_{22}H_{39}O_6$ 399.2744.

Acknowledgment. This work was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

JA9523505