3-Acyltetramic Acid Antibiotics. 3. An Approach to the Synthesis of Bu-2313†[1]

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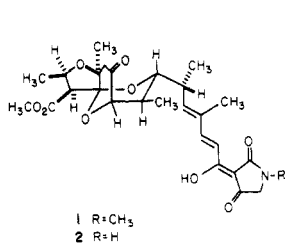
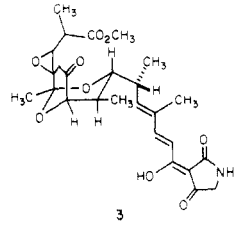
Received May 30, 1986

An approach to the synthesis of the bicyclononane portion of the 3-acyltetramic acid antibiotic Bu-2313 is presented. The highly unstable α-keto aldehyde obtained by Swern oxidation of the diol **23** was allowed to condense with the unreactive α-keto phosphoranylidene **17** affording the enedione **24**. The silyl ethyl was cleaved and the hydroxyl caused to add to the enedione in a five-exo fashion to form the tetrahydrofuran. The combination of functional groups necessary for ketal formation was investigated, showing that the system does not form the desired ketal in most circumstances (Table I). Given the correct functional group array, it was shown that the ketalization is more favorable with the stereochemistry of the natural product.

Members of the acyltetramic acid class of compounds, Bu-2313 A (**1**),[3] Bu-2313 B (**2**),[3] nocamycin (**3**),[4,5] tirandamycin (**4**),[6] and streptolydigin (**5**)[7] have aroused interest



1 R=CH₃
2 R=H



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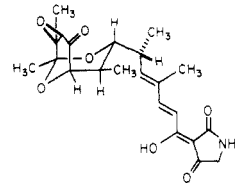

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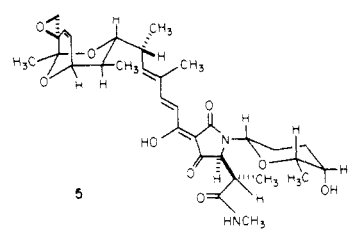

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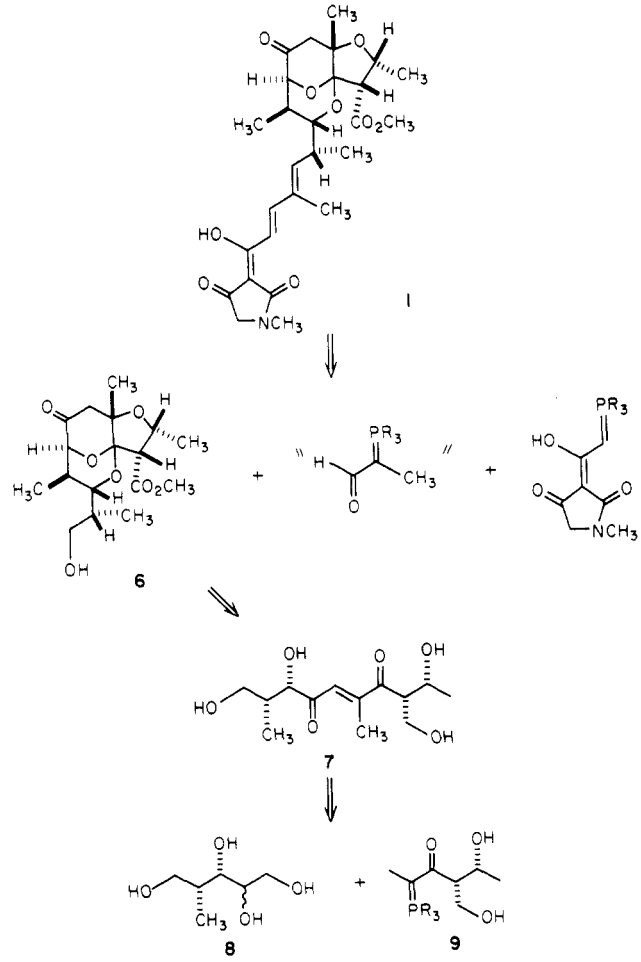
because of their significant biological activities and complex structures. Both streptolydigin and tirandamycin have been shown to inhibit RNA polymerase[8] and the process of oxidative phosphorylation.[9] The mode of action for Bu-2313 has not been determined but is presumably similar to that of tirandamycin and streptolydigin. These compounds differ from the simplet tetramic acids structurally and biologically.[10]

Synthetic routes to these antibiotics are of interest because of both their structural complexity and the potential value of structure–activity studies with analogues. The first two phases of this effort, syntheses of tirandamycic acid[11] and streptolic acid,[12] have been reported. Several other efforts directed at tirandamycin have been reported,[13] a number of which have culminated in successful total syntheses. As a continuation of the program in these laboratories we have undertaken a synthesis of Bu-2313.

The synthetic approach we envisioned (Scheme I) was designed to utilize the chemistry developed in our previous efforts.[11,12] However, it was clear that a significant digression would be necessary because formation of the tetrahydrofuran fused to the 2,9-bicyclononane in Bu-2313 was not compatible with the established strategy. We therefore proposed to apply the combination Swern oxidation–Wittig condensation procedure recently reported from the laboratories[14] to form an enedione (**7**), which

Scheme I. Retrosynthetic Analysis for Bu-2313



could be cyclized to form the tetrahydrofuran. We anticipated that the chain could then be extended and the

† Contribution 7410.

(1) Grateful acknowledgement is made for support of this investigation by a grant from NIH (GM-30335). Acknowledgement is also made for the use of the Midwest Center for Mass Spectrometry, University of Nebraska, and the University of California at Riverside Mass Spectrometry Lab for high-resolution mass spectra.

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(3) (a) Nakagawa, S.; Naito, T.; Kawaguchi, H. *Heterocycles* **1979**, *13*, 477–495. (b) Tsukiura, H.; Tomita, K.; Hanada, M.; Kobaru, S.; Tsunakawa, M.; Fujisawa, K.; Kawaguchi, H. *Antibiot.* **1980**, *33*, 157–165. (c) Tsunakawa, M.; Toda, S.; Okita, T.; Hanada, M.; Nakagawa, S.; Tsukiura, H.; Naito, T.; Kawaguchi, H. *Ibid.* **1980**, *33*, 166–172. (d) Toda, S.; Nakagawa, S.; Naito, T.; Kawaguchi, H. *Ibid.* **1980**, *33*, 173–181.

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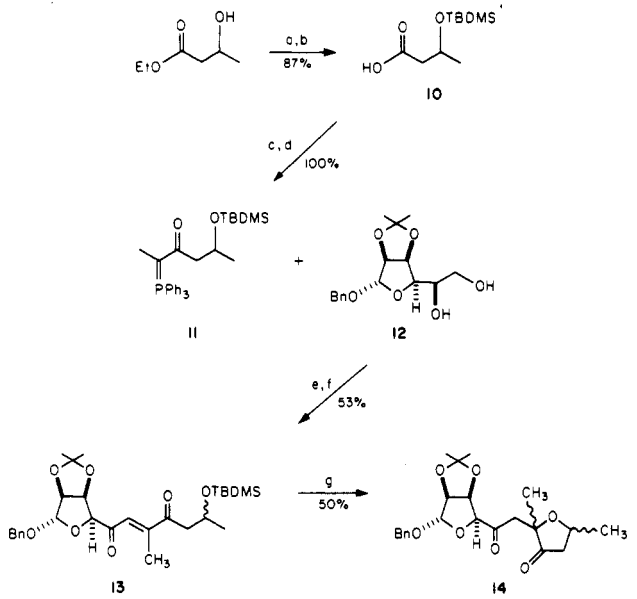
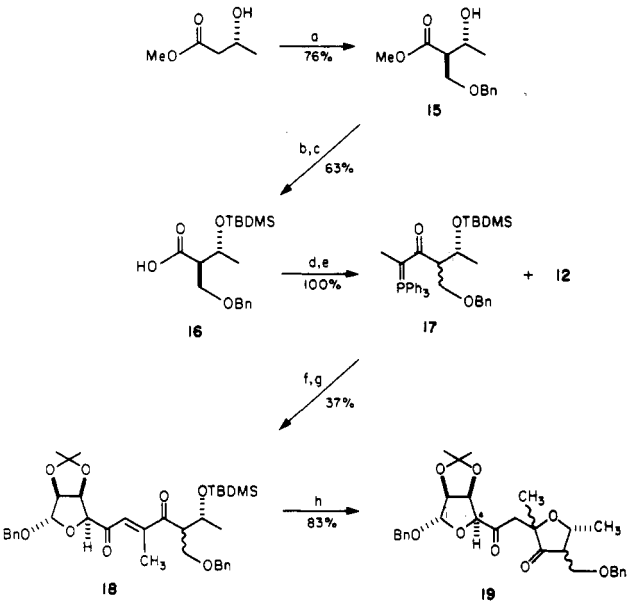
Scheme II. Wittig Reaction with an α-Keto Aldehyde and Closure[a]



[a] (a) TBSCl, imidazole, DMF. (b) 1 N NaOH, MeOH. (c) $(COCl)_2$, DMF, benzene. (d) $EtP^+Ph_3Br^-$, BuLi, benzene. (e) 12: $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2. (f) 11, CH_2Cl_2. (g) $LiBF_4$, TsOH, CH_2Cl_2, acetone.

Scheme III. Synthesis of the Chiral α-Keto Phosphoranylidene[a]



[a] (a) LDA, TFH; BOMCl, THF. (b) TBSCl, imidazole, DMF. (c) 1 N LiOH, MeOH. (d) $(COCl)_2$, DMF, benzene. (e) $EtP^+Ph_3Br^-$, BuLi, benzene. (f) 12: $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2. (g) 17, CH_2Cl_2. (h) $LiBF_4$, TsOH, CH_2Cl_2, acetone.

ketal formed, at which point the precedented route would be joined. Our efforts to prove the viability of this approach are the subject of this report.

The greatest concerns we had for the synthesis were whether reaction conditions could be found under which a stabilized Wittig reagent (**9**) would condense with the proposed α-keto aldehyde (from **8**) and whether the resultant enedione (**7**) would cyclize to form the furan. In order to allay the first of these concerns, a model system was investigated first (Scheme II). Treatment of the acid **10** with oxalyl chloride and catalytic *N,N*-dimethylformamide formed the acid chloride. Addition of the crude reaction mixture to 3 equiv of salt-free ethyl Wittig reagent afforded, after aqueous workup, the desired stabilized Wittig reagent **11**.[15] Similar compounds have been shown[16] to condense very slowly with unhindered aldehydes at elevated temperatures and not at all with ketones. Fortunately, the high reactivity of the α-keto aldehyde formed by Swern oxidation of the diol **12**[17] allowed the condensation with **11** to proceed at a reasonable rate at 0 °C to afford the enedione **13** as a mixture of diastereomers. Assignment of the indicated stereochemistry was based upon the ^1H NMR and UV spectra.[18]

It has been hoped that the alkoxide formed by removal of the *tert*-butyldimethylsilyl (TBDMS) group under standard conditions (tetra-*n*-butylammonium fluoride in THF) would spontaneously add to the enedione to form the desired tetrahydrofuran. Unfortunately this did not occur. A detailed investigation of this reaction provided conditions that produced the tetrahydrofuran **14** in moderate yield. The stereochemical outcome of this reaction was not rigorously determined since racemic material was used to form the model Wittig reagent. However, the reaction appeared to yield a mixture of four compounds, suggesting a nonspecific addition to the olefin. Successful formation of the tetrahydrofuran by this sequence of reactions was an encouraging result. The apparent lack of stereoselectivity in the addition reaction was disturbing,

(4) (a) Gauze, G. F.; Sveshnikova, M. A.; Ukholina, R. S.; Komarova, G. N.; Bazhanov, V. S. *Antibiotiki (Moscow)* **1977**, *22*, 483–486. (b) Brazhnikova, M. G.; Konstantinova, N. V.; Potapova, N. P.; Tolstykh, I. V. *Ibid.* **1977**, *22*, 486–489. (c) Horvath, G.; Brazhnikova, M. G.; Konstantinova, N. V.; Tolstykh, I. V.; Potapova, N. P. *J. Antibiot.* **1979**, *32*, 555–558.

(5) Comparison of the published spectral data for Bu-2313 B (ref 3a) and Nocamycin (ref 4b) leave little doubt that these two are in fact the same compound.

(6) (a) MacKellar, F. A.; Grostic, M. F.; Olsen, E. C.; Wnuk, R. J.; Branfman, A. R.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4943–4945. (b) Duchamp, D. J.; Branfman, A. R.; Button, A. C.; Rinehart, K. L., Jr. *Ibid.* **1973**, *95*, 4077–4078. (c) Hagenmeier, H.; Jaschke, K. H.; Santo, L.; Scheer, M.; Zaehner, H. *Arch. Microbiol.* **1976**, *109*, 65–74.

(7) (a) Rinehart, K. L., Jr.; Beck, J. R.; Epstein, W. W.; Spicer, L. D. *J. Am. Chem. Soc.* **1963**, *85*, 4035–4037. (b) Rinehart, K. L., Jr.; Borders, D. B. *Ibid.* **1963**, *85*, 4037–4038. (c) Rinehart, K. L., Jr.; Beck, J. R.; Borders, D. B.; Kinstle, T. H.; Kraus, D. *Ibid.* **1963**, *85*, 4038–4039. (d) Pearce, C. J.; Rinehart, K. L., Jr. *Antibiot.* **1983**, *36*, 1536–1538.

(8) Tirandamycin: Reusser, F. *Infect. Immun.* **1970**, *2*, 77–81. Streptolydigin: Siddhikol, C.; Erbstoeszer, J. W.; Weisblum, B. *J. Bacteriol.* **1969**, *99*, 151–155.

(9) Tirandamycin: Reusser, F. *Infect. Immun.* **1970**, *2*, 82–88. Streptolydigin: Reusser, F. *J. Bacteriol.* **1969**, *100*, 1335–1341.

(10) See, for example: Gitterman, C. O. *J. Med. Chem.* **1965**, *8*, 483–486.

(11) Ireland, R. E.; Wuts, P. G. M.; Ernst, B. *J. Am. Chem. Soc.* **1981**, *103*, 3205–3207.

(12) Ireland, R. E.; Smith, M. G., submitted for publication.

(13) (a) Schlessinger, R. H.; Bebernitz, G. R.; Lin, P.; Poss, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 1777–1778. (b) DeShong, P.; Ramesh, S.; Elango, V.; Perez, J. J. *Ibid.* **1985**, *107*, 5219–5224. (c) Martin, S. F.; Gluchowski, C.; Campbell, C. L.; Chapman, R. C. *J. Org. Chem.* **1984**, 2512–2513. (d) Kelly, T. R.; Chandrakumar, N. S. *Tetrahedron Lett.* **1985**, *26*, 2173–2176. (e) Ziegler, F. E.; Wester, R. T. *Ibid.* **1984**, *25*, 617–620. (f) Boeckman, R. K., Jr.; Thomas, A. J. *J. Org. Chem.* **1982**, *47*, 2823–2824. (g) Kelly, T. R.; Kaul, P. N. *Ibid.* **1983**, *48*, 2775–2777. (h) Danishefsky, S.; Harvey, D. F. *J. Am. Chem. Soc.*, **1985**, *107*, 6647–6652. (i) Neukom, C.; Richardson, D. P.; Myerson, J. H.; Bartlett, P. A. *J. Am. Chem. Soc.* **1986**, *108*, 5559–5568. (j) Boeckman, R. K.; Starrett, J. E.; Mickell, D. G.; Sum, P.-E. *J. Am. Chem. Soc.* **1986**, *108*, 5549–5559.

(14) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198–2200.

(15) (a) Bestmann, H. J.; Arnason, B. *Chem. Ber.* **1962**, *95*, 1513–1527. (b) Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 645–660.

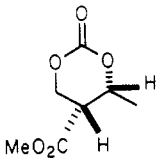
(16) Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1961**, 1266–1272.

(17) Brimacombe, J. S.; Hunedy, F.; Tucket, L. C. N. *Ibid.* **1968**, 1381–1384.

(18) The assignment of the stereochemistry about the double bond was made by comparing both the observed wavelength of maximal absorbance in the UV and the observed shift of the vinylic proton in the ^1H NMR with predicted values available in standard spectral textbooks.

but further study of this issue was deferred until chiral materials intermediates were used.

Analysis[19] of the retrosynthetic target, 1,9-dioxabicyclo[3.3.1]nonane, suggested that the thermodynamically most favorable stereochemistry of both the methyl ester and quaternary methyl centers was that of the natural product. We therefore predicted that these centers could be equilibrated to the desired configuration once the ketal had been formed. Thus, the main criterion for a chiral starting material for the Wittig reagent **9** was the stereochemistry at the secondary hydroxyl. For ease of compound identification, a single stereoisomer would be advantageous. A suitable candidate was methyl (*R*)-3-hydroxybutyrate, available in high enantiomeric purity[22] by depolymerization of the biopolymer poly((*R*)-3-hydroxybutyrate). Alkylation of the dianions of such β-hydroxy esters has been shown[23] to yield products of high diastereomeric excess with predictable stereochemistry. In this case, alkylation of the dianion with benzyloxymethyl chloride[24] (BOMCl) afforded the benzyl ether **15** (Scheme III) and the alternate diastereomer in a ratio of greater than 90:10 (capillary gas chromatography). The percent conversion in this reaction was always low (ca. 50%). Attempts to improve the efficiency by addition of excess BOMCl or by prolongation of the reaction time resulted in a lower yield of product. The product stereochemistry was proven through removal of the benzyl ether and formation of the cyclic carbonate I. The ^{1}H NMR spectrum of this rigid derivative was indicative of the assigned structure.



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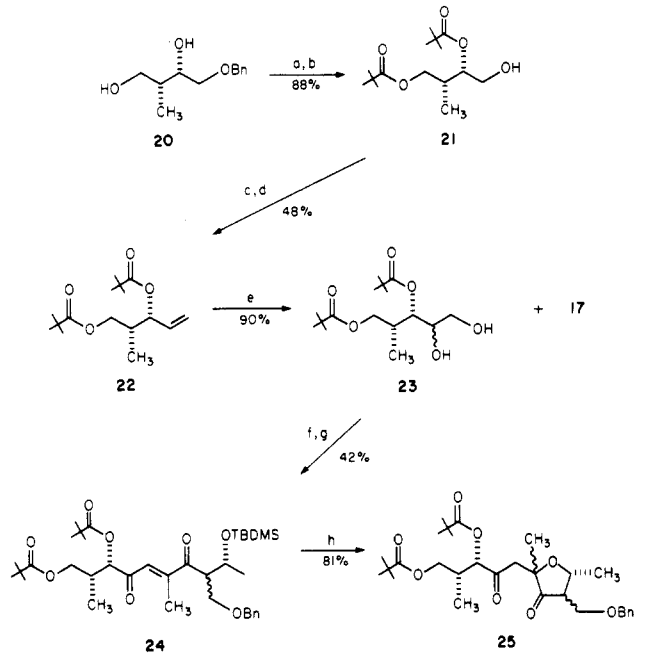
Protection of the secondary alcohol **15** with the silyl ether proceeded in high yield. Basic hydrolysis of the methyl ester was sluggish and was complicated by the production of two side products. These products arose from β-elimination of the benzyl ether and from epimerization of the α-center. Fortunately both byproducts could be separated from the desired acid (**16**) by careful chromatography. Formation of the Wittig reagent **17** under the conditions used previously afforded the desired material along with large amounts of β-elimination product. Attempted application of the thiopyridyl ester method of Overman[25] resulted in a higher percentage of β-elimination. In the end careful formation and workup of the acid

Scheme IV. Synthesis of an Acid Stable Protected 8 and Closure[a]



[a] (a) Pivaloyl chloride, DMAP, pyridine, CH_2Cl_2. (b) H_2, 10% Pd/C, EtOH. (c) $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2. (d) Tebbe's reagent, pyridine, benzene. (e) OsO_4, NMO, acetone, H_2O. (f) **23**: $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2. (g) **17**, CH_2Cl_2. (h) $LiBF_4$, TsOH, CH_2Cl_2, acetone.

chloride derived from the acid **16** followed by treatment with slightly less than 2 equiv of salt-free ethyl Wittig reagent was found to be the best means for the formation of the chiral-stabilized Wittig reagent **17**. Although the spectral evidence was inconclusive, it appeared that the stereochemistry at the center α to the ketone had been compromised during the reaction. This Wittig reagent (**17**) was used for a series of model experiments[26] similar to those above that showed that the stereochemical outcome of the tetrahydrofuran ring formation did not compromise the crucial chirality at C4.

Attention was then turned to the preparation of a suitable derivative of the retrosynthetic target tetrol **8** (Scheme I). Protection of the known[27] diol **20** as the bis(pivaloate) ester and hydrogenolysis of the benzyl ether afforded the alcohol **21** (Scheme IV). Oxidation to the aldehyde proceeded smoothly. Addition of benzyloxymethyllithium was predicted[28] to result in a mixture of compounds. An alternative strategy for this homologation would be to convert the aldehyde into the analogous olefin and then hydroxylate. Addition of a methyl Wittig reagent to the aldehyde afforded, at best, very low yields of the olefin. Olefination using Tebbe's reagent[29] afforded the desired olefin **22** in 48% unoptimized yield from the alcohol **22**.

The diol **23**, obtained from the olefin by catalytic osmium tetraoxide hydroxylation,[30] was submitted to the Swern–Wittig procedure as before but only gave a 10–15%

(19) Both models and force-field calculations[20,21] suggested that the natural configuration at the quaternary center would be highly favored. The natural configuration at the methyl ester center was predicted to be only slightly more favorable.

(20) For a general discussion of force-field calculations see: Burkert, U.; Alliger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(21) The particular program utilized was BIGSTRN-3: Buergi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1427–1438. BIGSTRN-3 predicted a 7-kcal energy difference between the two possible configurations at the quaternary methyl center and a 0.7-kcal energy difference at the methyl ester center, each favoring the natural configuration.

(22) Seebach, D.; Zueger, M. *Helv. Chim. Acta* **1982**, *65*, 495–503.

(23) (a) Frater, G. *Helv. Chim. Acta* **1979**, *62*, 2825–2832. (b) Seebach, D.; Wasmuth, D. *Ibid.* **1980**, *63*, 197–200.

(24) Connor, D. S.; Klein, G. W.; Taylor, G. N. *Org. Synth.* **1972**, *52*, 16–19 and references cited therein.

(25) Overman, L. E.; Bell, K. L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *u06*, 4192–4201.

(26) Wardle, R. B. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1986.

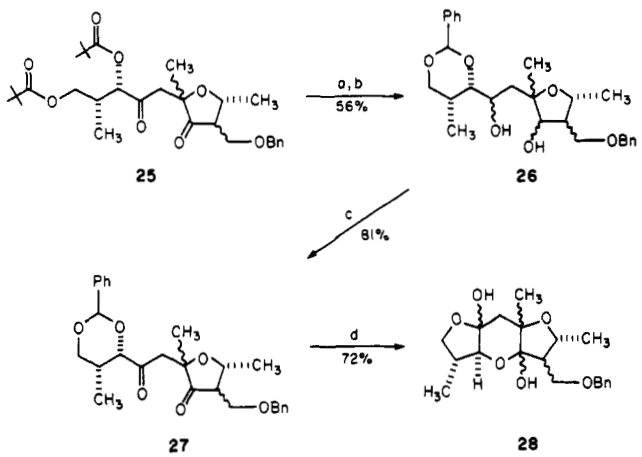
(27) Tius, M.; Fauq, A. H. *J. Org. Chem.* **1983**, *48*, 4131–4132. The immediate precursor to this diol is commercially available from Fluka Chemical Corp.

(28) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481–1487.

(29) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *Ibid.* **1980**, *102*, 3270–3272.

(30) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973–1976.

Scheme V. Deprotection of 31 by Reduction-Protection-Oxidation[a]



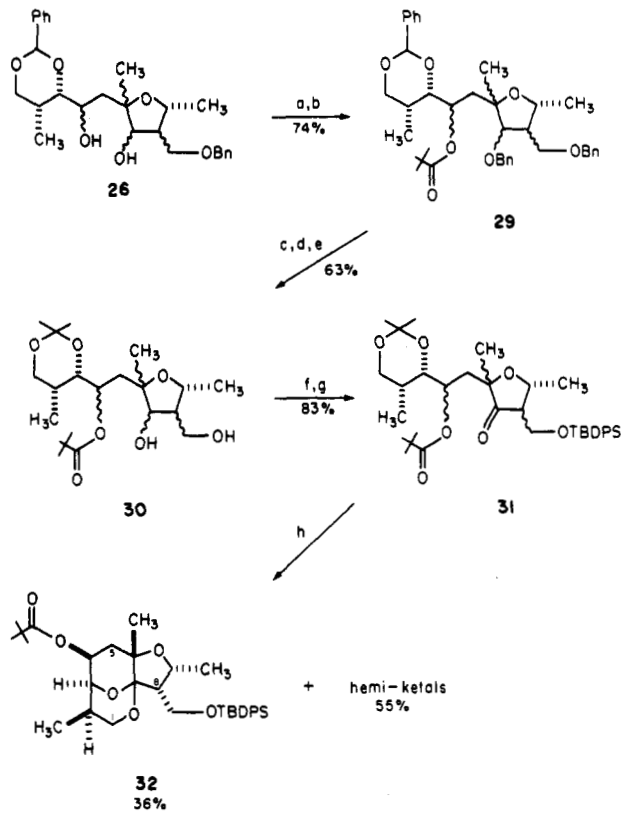
[a] (a) LAH, THF. (b) PhCHO, TsOH, benzene. (c) $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2. (d) 10% HCl, THF.

yield of the desired enedione **24**. Also obtained were the keto alcohol resulting from partial oxidation of **23**, large amounts of polymeric material (apparently from the α-keto aldehyde), and unreacted Wittig reagent. The yield of the enedione **24** was improved to 42% by allowing the activated dimethyl sulfoxide to react with the diol at −30 °C in order to facilitate the oxidation and by maintaining that temperature throughout the reaction to minimize polymerization. It was also shown at this time that an excess of the Wittig reagent was not necessary. As before, two diastereomers were obtained which were separated with difficulty. Their respective ^1H NMR spectra showed definitively that the stereochemistry of the α-center in the Wittig reagent **17** had indeed been scrambled. Because the separation of these two compounds was extremely tedious and because it was planned that this center would shortly be equilibrated to the thermodynamically most favorable configuration, the diastereomers were carried on as a mixture. Closure to the tetrahydrofuran **25** by the usual method proceeded in good yield and afforded what appeared to be two compounds. This observation suggests that some selectivity had occurred in the cyclization.

Reduction of **25** (Scheme V) with lithium tetrahydridoaluminate followed by treatment with benzaldehyde and catalytic acid[31] afforded the acetal **26**. Naturally, the intermediate tetrol and the acetal **26** as well as similar intermediates throughout the remainder of this effort were complex mixtures of diastereomers. The complete stereochemical identities of these mixtures were not elucidated fully. However, the alcohol resulting from reduction of the ring ketone possessed a syn relationship to the neighboring benzyloxymethyl substituent, and at no time did there appear to be more than four compounds in any of the product mixtures.

Because these compounds were mixtures, identification was a significant problem and a greater reliance was necessarily placed both on conversion of the intermediate products to more easily identifiable species and on combustion analysis. Because of these difficulties the structure of **26** was not firmly established until after Swern oxidation to the diketone **27**. The benzylidene acetal was surprisingly stable to attempt acidic hydrolysis but succumbed to 10% HCl. Not surprisingly, the product recovered from the hydrolysis was not the diol or the desired ketal, but

Scheme VI. Ketal Formation[a]



[a] (a) BaO, $Ba(OH)_2$, BnBr, DMF. (b) Pivaloyl chloride, DMAP, CH_2Cl_2. (c) 10% HCl, THF. (d) TsOH, DMP, acetone. (e) H_2, 10% Pd/C, HOAc, EtOAc. (f) TBDPSCl, DMAP, CH_2Cl_2. (g) $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2. (h) 10% HCl, THF.

the bis hemiketal **28**. However, it was very disappointing to find that this hemiketal could not be dehydrated to the desired ketal.

A solution to this complication appeared to be in the differentiation of the two ketones so that only the tetrahydrofuran ketone would be available for ketalization. The diol **26** (Scheme VI) already had the 1,3 diol protected and, if one of the remaining secondary alcohols could be selectively protected, the necessary differentiation would be accomplished. Several different protections were attempted, but only a benzyl group was incorporated selectively when a modification of the procedure of Paulsen[32] was used.

The location of the benzyl group in this product was not obvious but oxidation of the remaining free hydroxyl group to the ketone left no question that the tetrahydrofuran alcohol had been protected. That the tetrahydrofuran alcohol rather than the acyclic alcohol was protected was actually the less desirable result as in required substitution of an alternate protecting group for the benzylidene acetal because the 1,3-diol needed to remain protected while the benzyl ethers were cleaved. The remaining secondary alcohol was initially protected as the trimethylsilyloxymethyl (SEM)[33] or methoxymethyl (MOM)[34] ethers, but these groups were abondoned when they were found to hydrolyze at a rate similar to the benzylidene acetal. This alcohol was finally protected as the pivaloate ester (**29**). This protecting group was choosen for the stability that had made it problematic in earlier model studies.[26]

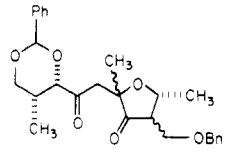
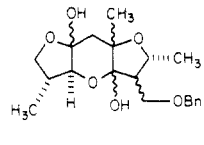
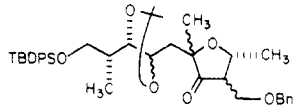
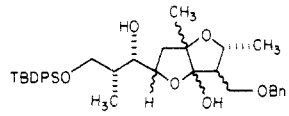
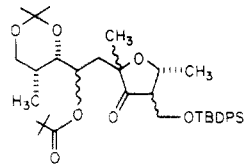
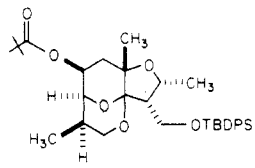
(31) Foster, A. B.; Haines, A. H.; Stacey, M. *Tetrahedron* **1961**, *16*, 177–184.

(32) Paulsen, H.; Lockhoff, O. *Chem. Ber.* **1981**, *114*, 3079–3101.

(33) Lipshutz, B. H.; Pegram, J. J. *Tetrahedron Lett.* **1980**, *21*, 3343–3346.

(34) Stork, G.; Takahashi, T. *J. Am. Chem. Soc.* **1977**, *99*, 1275–1276.

Table I. Summary of Ketal Formation Attempts

Starting Material	Product
 27	 28
	 ref 26
 31	 32

Cleavage of the benzylidene acetal proceeded at a reasonable rate with 3:1 THF/10% aqueous HCl only at 50 °C, conditions that are unusually vigorous.[35] Formation of the acetonide and hydrogenolysis of the benzyl ethers afforded the diol **30**. Therefore the primary alcohol was selectively protected as the TBDPS ether and the resultant monoalcohol was oxidized to afford the desired tetrahydrofuran ketone **31** with the acyclic ketone still blocked. Acidic hydrolysis of the acetonide[36] provided a single ketal **32** as the major product along with three hemiketals, none of which could be dehydrated to a ketal.[37]

It was with great satisfaction that we discovered upon extensive ^{1}H NMR investigation that this ketal had the stereochemistry of the natural product at all the established stereocenters. The key evidence came in the form of nuclear Overhauser effect experiments which verified that the C2 and C6 methyl groups as well as the C8 proton of the ketal **32** were all on one "face" of the molecule (see Experimental Section). The exclusive formation of the "natural" ketal partially[38] verified our prediction that this configuration would be energetically the most favorable.

As a result of this foregoing synthesis and the investigation of several earlier model systems used to evaluate appropriate blocking groups and the ease of bicyclic ketal formation, and interesting observation on intramolecular ketal formation can be made (Table I). Acid treatment of each starting material shown led to different structural ketals or hemiketals depending on the disposition and character of side-chain functionality. In the first two cases the result can be rationalized by kinetically more favorable five-ring hemiketal formation first. In the last case, only six-ring hemiketal formation can occur and the desired bicyclic system results.

Experimental Section[39]

Ethyl 3-(*tert*-Butyldimethylsiloxy)butyrate. To a stirred solution of 2.50 g (18.9 mmol) of ethyl 3-hydroxybutyrate in 50 mL of *N,N*-dimethylformamide were added 3.60 g (23.9 mmol) of *tert*-butylchlorodimethylsilane and 3.4 g (49.9 mmol) of imidazole. After 8 h, the reaction mixture was diluted with 200 mL of ether and 50 mL of 5% aqueous HCl. The phases were separated, and the organic phase was extracted with 50 mL of water and then 50 mL of saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$), and then the solvent was removed under reduced pressure to yield 4.66 g (100%) of the desired silyl ether as a colorless oil: R_f = 0.56 (1:1 petroleum ether/ether); IR ($CHCl_3$) 2940, 2880, 2850, 1770, 1450, 1380, 1300, 1180, 1130, 1080, 1030, 1000, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6 H, $(CH_3)_2Si$), 0.82 (s, 9 H, $(CH_3)_3C$), 1.18 (d, 3 H, CH_3C, J = 6 Hz), 1.21 (t, 3 H, CH_3CH_2, J = 7 Hz), 2.38 (2d, 2 H, $CH_2C{=}O$, J = 6 Hz), 4.10 (q, 2 H, CH_2O, J = 7 Hz), 4.20 (sextet, 1 H, HCO, J = 6 Hz).

3-(*tert*-Butyldimethylsiloxy)butyric Acid (10). To a stirred solution of 4.0 g (16.3 mmol) of the above ester in 150 mL of methanol was added 60 mL of 1 N aqueous NaOH. After 20 h, the reaction mixture was diluted with 100 mL of ether, and the phases were separated. The aqueous phase was acidified to pH 2 and extracted with three portions of 200 mL of ether. The combined organics were dried ($MgSO_4$) and concentrated under reduced pressure to afford 3.1 g (87.1%) of the acid **10** as a colorless oil: R_f = 0.47 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3300–2400 (br), 1710, 1460, 1410, 1380, 1300, 1250, 1135, 1090, 1005, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 6 H, $(CH_3)_2Si$), 0.85 (s, 9 H, $(CH_3)_3C$), 1.18 (d, 3 H, CH_3C, J = 6 Hz), 2.48 (d, 2 H, CH_2, J = 6 Hz), 4.28 (sextet, 1 H, HCO, J = 6 Hz), 8.7 (br s, 1 H, COOH). To a small portion of the product in ether was added excess ethereal diazomethane. After 15 min, the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with 98:2 petroleum ether/ether to afford an analytically pure sample of the methyl ester of **10**: R_f = 0.30 (95:5 petroleum ether/ether); IR ($CHCl_3$) 2945, 2925, 2885, 2850, 1725, 1460, 1435, 1375, 1300, 1250, 1180, 1130, 1085, 1005, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00, 0.02 (2s, 6 H, $(CH_3)_2Si$), 0.83 (s, 9 H $(CH_3)_3C$), 1.15 (d, 3 H, CH_3C, J = 6 Hz), 2.38 (d, 2 H, CH_2, J = 6 Hz), 3.70 (s, 3 H, CH_3O), 4.22 (sextet, 1 H, HCO, J = 6 Hz).

(35) See ref 31 and: Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981; pp 141–151.

(36) This acetonide was completely hydrolyzed in 1 h, while the corresponding benzylidene acetal required about 24 h at 50 °C using the same mixture of 1:3 10% aqueous HCl/THF.

(37) Two of the hemiketals could be converted under acid catalysis to a single compound (see Experimental Section) which was also a hemiketal. Nuclear Overhauser effect experiments failed to provide information about the stereochemistry of this compound or the other hemiketal formed during the hydrolysis.

(38) More complete verification would require that all possible stereoisomers at the centers in question be submitted to these reaction conditions. Since we were submitting a mixture of only three compounds (determined by the number of products) and could state the stereochemistry of only one of them (the ketal) with certainty, our result shows only that the desired configuration is relatively favorable.

(39) *General Information*: Proton nuclear magnetic resonance spectra were recorded with a Varian EM-390 spectrometer at 90 MHz unless otherwise specified. 400 MHz refers to a spectrum recorded with a JEOL JNM-GX400, and 200 MHz refers to a spectrum recorded with a Varian XL-200. Data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (multiplicity, integrated relative intensity, assignment, coupling constants). Optical rotations were measured with a Jasco DIP-181 polarimeter in a 1-dm cell of 1-mL capacity; chloroform for these measurements was filtered through activity III alumina immediately prior to use. Infrared spectra were recorded with a Perkin-Elmer 1310 spectrometer. Ultraviolet spectra were recorded with a Beckman 25 spectrometer. Capillary gas chromatography was performed with a Hewlett-Packard 5890A gas chromatograph on columns from J & W Scientific by using prescribed flow conditions. Data are reported as follows: (column, temperature program) retention times, ratio. Reaction solvents and liquid reagents were purified by distillation or dried over appropriate agents prior to use. Reactions were run under an atmosphere of argon that had been dried by passage through a drying tower filled with anhydrous $CaSO_4$. Reaction flasks were flame-dried when possible and always purged with argon and evacuated under high vacuum several times by using a manifold system. Syringes and reaction flasks were dried at least 12 h in an oven (120–140 °C) and cooled in a desiccator over anhydrous $CaSO_4$ prior to use. Elemental analyses were performed by Spang Microanalytical Laboratory, Star Route 1, Box 142, Eagle Harbor, MI 49951. High-resolution mass spectra were performed by the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE 68588-0362, or the University of California at Riverside Mass Spectrometry Lab.

Anal. Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found: C, 56.87; H, 10.31.

5-(*tert*-Butyldimethylsiloxy)-2-(triphenylphosphoranylidene)-3-hexanone (11). To a stirred solution of 1.8 g (8.24 mmol) of the acid **10** in 25 mL of benzene were added 50 μL (0.65 mmol) of *N,N*-dimethylformamide and then 0.74 mL (8.48 mmol) of oxalyl chloride. After 1 h, the reaction mixture was added via cannula over 6 min to the supernatant centrifugate of 9.2 g (24.8 mmol) of ethyltriphenylphosphonium bromide and 10.3 mL of 2.4 M *n*-butyllithium in hexanes in 105 mL of benzene at 80 °C. After 10 min, the reaction mixture was allowed to cool to room temperature and was diluted with 300 mL of ether and 75 mL of 10% aqueous K_2CO_3. The phases were separated and the aqueous phase was extracted with 100 mL of ether. The combined organics were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was diluted with 300 mL of ether and then extracted with two portions of 75 mL of 10% aqueous K_2CO_3. The organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure to afford 4.1 g (100%) of the α-keto phosphoranylidene **11** as a red oil: IR ($CHCl_3$) 3030, 2955, 2930, 2850, 1720, 1500, 1435, 1380, 1255, 1170, 1110, 1100, 990, 840, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H, $(CH_3)_2Si$), 0.80 (s, 9 H, $(CH_3)_3C$), 1.18 (d, 3 H, CH_3C, J = 6 Hz), 1.58 (d, 3 H, $CH_3C{=}P$, J = 18 Hz), 2.46 (d, 2 H, CH_2, J = 6 Hz), 4.1–4.2 (m, 1 H, HCO), 7.2–7.9 (m, 15 H, PhH).

(10ξ)-Benzyl (*E*)-10-*O*-(*tert*-Butyldimethylsilyl)-6,7,9,11-tetradeoxy-2,3-*O*-isopropylidene-7-methyl-α-D-*lyxo*-undec-6-enofuranosido-5,8-diulose (13). To a stirred solution of 0.60 mL (6.91 mmol) of oxalyl chloride in 6 mL of dichloromethane at −78 °C was added a solution of 0.58 mL (8.16 mmol) of dimethyl sulfoxide in 3 mL of dichloromethane. After 12 min, a solution of 597.3 mg (3.14 mmol) of the diol **12** in 8.0 mL of dichloromethane was added to the reaction mixture over 3.5 min. After 15 min, 2.19 mL (15.70 mmol) of triethylamine was added and, after 15 min at −78 °C, a solution of 3.0720 g (6.26 mmol) of the α-keto phosphoranylidene **11** in 14 mL of dichloromethane was added over 5 min. The reaction mixture was allowed to warm to 0 °C. After 45 min, the reaction mixture was diluted with 200 mL of ether and 50 mL of saturated aqueous NaCl. The phases were separated, and the organic phase was dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue chromatographed on 60 g of silica gel with 9:1 petroleum ether/ether to afford 860.2 mg (52.7%) of the desired enedione **13** as a colorless oil: R_f = 0.57 (1:1 petroleum ether/ether); evaporative distillation 195 °C (0.05 mmHg); IR ($CHCl_3$) 3030, 2950, 2930, 2850, 1780, 1685, 1610, 1460, 1380, 1255, 1090, 1035, 1000, 840 cm^{-1}; UV (methanol) λ_{max} = 247 nm, ε = 13 000; ^1H NMR ($CDCl_3$) δ 0.01, 0.01 (2s, 6 H, $(CH_3)_2Si$), 0.82 (s, 9 H, $(CH_3)_3C$), 1.16 (d, 3 H, CH_3COSi, J = 6 Hz), 1.20, 1.32 (2s, 6 H, $(CH_3)_2C$), 2.14 (s, 3 H, $CH_3C{=}C$), 2.6–2.7 (m, 2 H, $CH_2C{=}O$), 4.4–4.7 (m, 5 H, HCO, CH_2Ph), 4.98 (2d, 1 H, $CHC{=}O$, J = 5 Hz, J' = 4.5 Hz) 5.20 (s, 1 H, CHOBn), 7.10 (s, 1 H, $HC{=}C$), 7.26 (s, 5 H, PhH). Anal. Calcd for $C_{28}H_{42}O_7Si$: C, 64.83; H, 8.16. Found: C, 64.84; H, 8.02.

Benzyl (7ξ,10ξ)-7,10-Anhydro-6,9,11-trideoxy-2,3-*O*-isopropylidene-7-*C*-methyl-α-D-*lyxo*-undecafuranosido-5,8-diulose (14). To a stirred solution of 76.5 mg (0.15 mmol) of the enedione **13** in 2.6 mL of 1:1 acetone/dichloromethane were added 110 mg (1.17 mmol) of lithium tetrafluoroborate and 55 mg (0.29 mmol) of *p*-toluenesulfonic acid. After 3.5 h, the reaction was diluted with 2 mL of carbon tetrachloride and directly chromatographed on 10 g of silica gel with 4:1 petroleum ether/ether to afford 29.7 mg (49.8%) of the furanone **14** as a colorless oil: R_f = 0.35 (1:1 petroleum ether/ether); evaporative distillation 180–185 °C (0.05 mmHg); IR ($CHCl_3$) 2920, 2850, 1755, 1725, 1455, 1385, 1080, 1030, 970, 870 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 1.24, 1.25, 1.26, 1.27 (4s, 6 H, $(CH_3)_2C$), 1.32–1.40 (m, 3 H, CH_3CO), 1.39, 1.41 (2s, 3 H, $CH_3CC{=}O$), 2.2–3.4 (m, 4 H, $CH_2C{=}O$), 4.32–4.34 (m, 1 H, $CHCH_3$), 4.45–4.67 (m, 4 H, CH_2O, OCHCHO), 4.98–5.02 (m, 1 H, $CHC{=}O$), 5.20 (d, 1 H, CHOBn, J = 6 Hz), 7.24–7.33 (m, 5 H, PhH). Anal. Calcd for $C_{22}H_{28}O_7$: C, 65.33; H, 6.98. Found: C, 65.38; H, 6.82.

(2*R*,3*R*)-Methyl 2-[(Benzyloxy)methyl]-3-hydroxybutyrate (15). To a stirred solution of 11.8 mL (84.4 mmol) of diisopropylamine and 41.0 mL of 2.06 M *n*-butyllithium in 160 mL of tetrahydrofuran at −78 °C was added a solution of 3.99 g (33.8 mmol) of methyl (*R*)-3-hydroxybutyrate[22] in 80 mL of tetrahydrofuran over 6 min. After 55 min, a solution of 5.2 mL (37.4 mmol) of benzyl chloromethyl ether in 36 mL of tetrahydrofuran was added to the reaction mixture over 3 min. The reaction mixture was allowed to warm to 0 °C. After 4 h, 100 mL of saturated aqueous NH_4Cl was added followed by 400 mL of ether and 50 mL of water. The phases were separated, and the aqueous phase was extracted with 400 mL of ether. The combined organic extracted were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was flash chromatgraphed on silica gel by using 3:2 petroleum ether/ether to afford 3.3984 g (42.2%) of the benzyl ether **15** and 1.78 g of starting material (76.2% based on unrecovered starting material). The product was a colorless oil: R_f = 0.38 (ether); evaporative distillation 95–100 °C (0.008 mmHg); $[\alpha]^{21}_D$ −8.0° (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3530, 3010, 2950, 2920, 2870, 1730, 1455, 1440, 1370, 1270, 1225, 1180, 1100, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (d, 3 H, CH_3C, J = 6.5 Hz), 2.75 (q, 1 H, $CHC{=}O$, J = 6 Hz), 2.81 (br s, 1 H, OH), 3.74 (s, 3 H, $CH_3OC{=}O$), 3.76 (abx, 1 H, HCHO, J = 9.4, 6.0 Hz), 3.77 (abx, 1 H, HCHO, J = 9.4, 6.0 Hz), 4.13 (dq, 1 H, CHOSi, J = 6.0, 6.5 Hz), 4.51 (ab, 1 H, HCHPh, J = 11.6 Hz), 4.52 (ab, 1 H, CHCPh, J = 11.6 Hz), 7.25–7.4 (m, 5 H, PhH); capillary GC (DB1701, 120 °C 2 min, 10 °C/min to 180 °C) major = 12.13 min, minor = 12.31 min, ratio = 14.0:1. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.52; H, 7.67.

(2*R*,3*R*)-2-Carbomethoxybutane-1,3-diol Cyclic Carbonate (I). To a stirred solution of a small portion of the benzyl ether **15** in ethyl acetate was added a small amount of 10% palladium on carbon. The reaction mixture was stirred under a hydrogen atmosphere for 24 h. The catalyst was removed by filtration, and the solvent was removed under reduced pressure. To the residue dissolved in 1 mL of benzene were added 0.5 mL of pyridine and then 4 mL of a solution of phosgene in benzene. After 1 h, the reaction mixture was diluted with 85 mL of ether and 15 mL of 10% aqueous HCl. The phases were separated, and the organic phase was dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was chromatographed on 1 g of silica gel with ether to afford the carbonate I as a colorless oil: R_f = 0.14 (ether); ^1H NMR ($CDCl_3$) 400 MHz δ 1.44 (d, 3 H, CH_3C, J = 6.6 Hz), 3.14 (ddd, 1 H, CHC, J = 6.5, 5.0, 4.2 Hz), 3.77 (s, 3 H, CH_3O), 4.50 (abx, 1 H, HCH, J = 11.6, 5 Hz), 4.62 (abx, 1 H, HCH, J = 11.6, 6.5 Hz), 4.84 (dq, 1 H HCO, J = 4.2, 6.6 Hz).

Methyl (2*R*,3*R*)-2-[(Benzyloxy)methyl]-3-(*tert*-butyldimethylsiloxy)butyrate. To a stirred solution of 24.9 g (97.7 mmol) of the alcohol **15** in 250 mL of *N,N*-dimethylformamide were added 19.8 g (131.4) of *tert*-butylchlorodimethylsilane and 18.0 g (264.4 mmol) of imidazole. After 3 h, the reaction mixture was diluted with 750 mL of ether and 150 mL of 10% aqueous HCl. The phases were separated, and the organic phase was extracted with two portions of 150 mL of water and one portion of 100 mL of saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was flash chromatographed by using 9:1 petroleum ether/ether to afford 29.6 g (85.9%) of the desired silyl ether as a colorless oil: R_f = 0.15 (95:5 petroleum ether/ether); evaporative distillation 100–105 °C (0.04 mmHg); $[\alpha]^{21}_D$ −8.95 (*c* 1.62, $CHCl_3$); IR ($CHCl_3$) 2950, 2930, 2850, 1730, 1455, 1440, 1380, 1365, 1255, 1100, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.0 (s, 6 H, $(CH_3)_2Si$), 0.82 (s, 9 H, $(CH_3)_3C$), 1.12 (d, 3 H, CH_3, J = 6 Hz), 2.7–2.8 (m, 1 H, CHC), 3.6–3.7 (m, 2 H, CH_2O), 3.74 (s, 3 H, CH_3O), 4.03 (dq, 1 H, CHOSi, J = 6, 6 Hz), 4.43 (s, 2 H, CH_2Ph), 7.24 (s, 5 H, PhH); capillary GC (DB1701, 120 °C 2 min, 10 °C/min to 200 °C) major = 14.74, minor = 14.24, ratio = 9.8:1. Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 64.80; H, 9.06.

(2*R*,3*R*)-2-[(Benzyloxy)methyl]-3-(*tert*-butyldimethylsiloxy)butyric Acid (16). To a stirred solution of 3.0 g (8.51 mmol) of the above ester in 90 mL of methanol was added 30 mL of 1 N aqueous lithium hydroxide. After 81 h, the methanol was removed under reduced pressure and the reaction mixture was acidified to pH 2. The reaction mixture was extracted with four portions of 150 mL of ether, and then the combined organic extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was chromatographed on 250 g of Silicar CC-4 special silica gel to afford 2.1 g (72.9%) of the acid **16** as a colorless oil: R_f = major 0.32, minor 0.22; IR ($CHCl_3$) 3530–2400 (br), 2950, 2930, 2850, 1750, 1710, 1450, 1380, 1360,

1255, 1100, 1025, 960, 840, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 6 H, $(CH_3)_2Si$), 0.81 (s, 9 H, $(CH_3)_3C$), 1.15 (d, 3 H, CH_3C, J = 6 Hz), 2.7–2.8 (m, 1 H, CHC), 3.62 (d, 2 H, CH_2O, J = 6.5 Hz), 4.1–4.2 (m, 1 H, HCO), 4.44 (s, 2 H, CH_2Ph), 7.24 (s, 5 H, PhH), 8.06 (br s, 1 H, CO_2H). A small portion of the acid before chromatography was treated with excess ethereal diazomethane to afford a sample for capillary GC (DB1701, 120 °C 2 min, 10 °C/min to 200 °C) major = 14.85, minor = 14.43, ratio = 3.36:1.

(3ξ)-(2*R*)-2-[(Benzyloxy)methyl]-3-(*tert*-butyldimethylsiloxy)-5-(triphenylphosphoranylidene)-4-hexanone (17). To a stirred solution of 786.9 mg (2.32 mmol) of the acid **16** in 15 mL of benzene were added 5 drops of *N,N*-dimelthylformamide and then 0.22 mL (2.52 mmol) of oxalyl chloride. After 25 min, the solvent was removed under reduced pressure, and then the residue was diluted with 10 mL of benzene and the solvent once again removed under reduced pressure. The dilution–solvent removal sequence was repeated, and then the residue was diluted with 40 mL of ether and filtered through dry Celite. The solvent was removed under reduced pressure, and the residue was dissolved in 16 mL of benzene and then warmed to 80 °C. To a slurry of 1.89 g (5.09 mmol) of ethyltriphenylphosphonium bromide in 36 mL of benzene was added 2.10 mL of 2.02 M *n*-butyllithium in hexane. After 30 min, the slurry was centrifuged. The supernatant red solution was transferred into the acid chloride solution via cannula over 6 min. After 30 min, the reaction was allowed to cool to room temperature and then diluted with 400 mL of ether and 75 mL of 10% aqueous K_2CO_3. The phases were separated, and the organic phase was dried ($MgSO_4$). The solvent was removed under reduced pressure to afford 1.4210 g (100%) of the α-keto phosphoranylidene **17** as a red oil: IR ($CHCl_3$) 3060, 2950, 2920, 2850, 1720, 1490, 1435, 1380, 1255, 1170, 1110, 1075, 1030, 1000, 840, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02, 0.04, (2s, 6 H, $(CH_3)_2Si$), 0.87 (s, 9 H, $(CH_3)_3C$), 1.09 (d, 3 H, CH_3C, J = 6 Hz), 1.68 (d, 3 H, $CH_3C{=}P$, J = 17 Hz), 2.3–2.4 (m, 1 H, CHC), 3.7–4.8 (m, 5 H, HCO, H_2CO), 7.2–7.9 (m, 20 H, PhH).

(9ξ)-Benzyl (*E*)-9-[(Benzyloxy)methyl]-10-*O*-(*tert*-butyldimethylsilyl)-6,7,9,11-tetradeoxy-2,3-*O*-isopropylidene-7-*C*-methyl-D-*glycero*-α-D-*lyxo*-undec-6-enofuranosido-5,5-diulose (18). To a stirred solution of 53 μL (0.61 mmol) of oxalyl chloride in 3.0 mL of dichloromethane at −78 °C was added 49 μL (0.69 mmol) of dimethyl sulfoxide. After 15 min, a solution of 85.8 mg (0.28 mmol) of the diol **12** in 4.0 mL of dichloromethane was added to the reaction mixture over 2 min. After 27 min, 0.19 mL (1.36 mmol) of triethylamine was added over 0.5 min. After 20 min, a solution of 844.5 mg (1.38 mmol) of the α-keto phosphoranylidene **17** in 5.0 mL of dichloromethane was added to the reaction mixture over 5 min. After 5 min, the reaction mixture was allowed to warm to 0 °C. After 1 h, the reaction mixture was diluted with 200 mL of ether and 20 mL of saturated aqueous NaCl. The organic phase was separated and dried ($MgSO_4$), and then the solvent was removed under reduced pressure. The residue was chromatographed on 10 g of silica gel with 9:1 petroleum ether/ether to afford 65.4 mg (37%) of the enedione **18** as a colorless oil: R_f = 0.56 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3020, 2960, 2930, 2850, 1710, 1680, 1610, 1380, 1365, 1260, 1100, 1085, 1035, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02, 0.07 (2s, 6 H, $(CH_3)_2Si$), 0.78, 0.82 (2s, 9 H, $(CH_3)_3C$), 1.09 (d, 3 H, CH_3COSi, J = 6 Hz), 1.18, 1.30 (2s, 6 H, $(CH_3)_2C$), 2.01, 2.15 (2s, 3 H, $CH_3C{=}C$), 3.0–3.1 (m, 1 H, CHC=O), 3.4–4.7 (m, 9 H, OCH, H_2CO), 4.92 (2d, 1 H, HCO, J = 5 Hz), 5.16 (br s, 1 H, CHOBn), 7.07 (s, 1 H, CH=C), 7.25 (s, 10 H, PhH). Anal. Calcd for $C_{36}H_{50}O_8Si$: C, 67.88; H, 7.89. Found: C, 67.76; H, 7.80.

(7ξ,9ξ)-Benzyl 7,10-Anhydro-9-[(benzyloxy)methyl]-6,9,11-trideoxy-2,3-*O*-isopropylidene-7-*C*-methyl-D-*glycero*-α-D-*lyxo*-undecofuranosido-5,8-diulose (19). To a stirred solution of 13.3 mg (0.021 mmol) of the enedione **18** in 0.4 mL of 1:1 acetone/dichloromethane were added 22.0 mg (0.235 mmol) of lithium tetrafluoroborate and 0.8 mg (0.042 mmol) of *p*-toluenesulfonic acid. After 3 h, the reaction was diluted with 0.5 mL of carbon tetrachloride and directly chromatographed on 5 g of silica gel with 4:1 petroleum ether/ether to afford 9.1 mg (83.3%) of the furanone **19** as a colorless oil: R_f = 0.42 (1:1 petroleum ether/ether); evaporative distillation 220–225 °C (0.03 mmHg); IR ($CHCl_3$) 3040, 3000, 2970, 2930, 2860, 1755, 1720, 1455, 1390, 1380, 1365, 1230, 1165, 1090, 1030, 980, 870, 705 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 1.17, 1.23, 1.25, 1.29 (4s, 6 H, $(CH_3)_2C$), 1.36, 1.38 (2s, 3 H, CH_3), 1.41, 1.45 (2d, 3 H, CH_3CH, J = 4.6 Hz, J' = 6.1 Hz), 2.56, 2.57 (2ddd, 1 H, CHC=O, J = 9.5, 7.8, 3.9 Hz, J' = 9.5, 4.6, 3.1 Hz), 2.96 (ab, 0.5 H, HCHC=O, J = 17.8 Hz), 3.04 (ab, 0.5 H, HCHC=O, J = 17.2 Hz), 3.07 (ab, 0.5 H, HCHC=O, J = 17.2 Hz), 3.18 (ab, 0.5 H, HCHC=O, J = 17.8 Hz), 3.61 (abx, 0.5 H, HCHOBn, J = 9.7, 3.1 Hz), 3.81 (abx, 0.5 H, HCHOBn, J = 9.7, 4.6 Hz), 3.92 (abx, 0.5 H, HCHOBn, J = 18, 7.8 Hz), 3.98 (abx, 0.5 H, HCHOBn, J = 18, 3.9 Hz), 4.32, 4.35 (2dq, 1 H, $HCCH_3$, J = 9.5, 4.6 Hz, J' = 9.5, 6.1 Hz), 4.4–4.7 (m, 6 H, CHOCOCH, CH_2Ph), 4.93, 5.03 (2dd, 1 H, OCHC=O, J = 6.2, 4.7 Hz, J' = 6.2, 5.0 Hz), 5.20 (d, 1 H, CHOBn, J = 3.4 Hz), 7.2–7.4 (m, 10 H, PhH). Anal. Calcd for $C_{30}H_{36}O_8$: C, 68.69; H, 6.97. Found: C, 68.85; H, 7.00.

1-*O*-Benzyl-3-deoxy-3-methyl-D-threitol Dipivaloate. To a stirred solution of 657.0 mg (3.12 mmol) of the diol **20** in 6.0 mL dichloromethane were added 1.55 mL (19.2 mmol) of pyridine, 1.15 mL (9.34 mmol) of pivaloyl chloride, and 76.3 mg (0.62 mmol) of *N',N'*-dimethylaminopyridine. After 24 h, the reaction mixture was diluted with 100 mL of ether and extracted successively with two portions of 25 mL of 10% aqueous HCl, 25 mL of saturated aqueous $NaHCO_3$, and 25 mL of water. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography on silica gel with 9:1 petroleum ether/ether afforded 1.1503 g (97.3%) of the desired diester as a colorless oil: R_f 0.38 (9:1 petroleum ether/ether); evaporative distillation 140 °C (0.05 mmHg); $[\alpha]^{21}_D$ −6.15° (*c* 1.74, $CHCl_3$); IR ($CHCl_3$) 2995, 2950, 1710, 1470, 1415, 1280, 1150, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, 3 H, CH_3, J = 6 Hz), 1.15 (s, 18 H, $(CH_3)_3C$), 2.2–2.3 (m, 1 H, CHC), 3.51 (d, 2 H, CH_2OBn, J = 5 Hz), 3.90 (d, 2 H, $CH_2OC{=}O$, J = 6 Hz), 4.46 (s, 2 H, CH_2Ph), 5.09 (q, 1 H, HCO, J = 5 Hz), 7.24 (s, 5 H, PhH). Anal. Calcd for $C_{22}H_{34}O_5$: C, 69.81; H, 9.05. Found: C, 69.66; H, 8.92.

3-Deoxy-3-methyl-D-threitol 2,4-Dipivaloate (21). To a stirred solution of 996.0 mg (2.63 mmol) of the above benzyl ether in 19.5 mL of absolute ethanol was added 850 mg of 10% palladium on carbon. The reaction mixture was agitated under 50 psi of hydrogen for 18 h. The catalyst was removed by filtration and the solvent was removed under reduced pressure. The residue was flash chromatographed with 2:1 petroleum ether/ether to afford 683.1 mg (90%) of the alcohol **21** as a colorless oil: R_f 0.28 (1:1 petroleum ether/ether); evaporative distillation 95–100 °C (0.04 mmHg); $[\alpha]^{21}_D$ −7.11° (*c* 1.435, $CHCl_3$); IR ($CHCl_3$) 3490 (br), 2970, 2890, 1710, 1475, 1455, 1395, 1365, 1280, 1155, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (d, 3 H, CH_3, J = 6 Hz), 1.15 (s, 18 H, $(CH_3)_3C$), 2.1–2.2 (m, 2 H, CHC, OH), 3.72 (t, 2 H, CH_2OH, J = 5 Hz), 3.94 (d, 2 H, $CH_2OC{=}O$, J = 6 Hz), 4.90 (q, 1 H, CHOC=O, J = 5 Hz). Anal. Calcd for $C_{15}H_{28}O_5$: C, 62.47; H, 9.79. Found: C, 62.30; H, 9.70.

3-Deoxy-3-methyl-D-threose Dipivaloate. To a stirred solution of 0.18 mL (2.06 mmol) of oxalyl chloride in 10.0 mL dichloromethane at −78 °C was added 0.30 mL (4.23 mmol) of dimethyl sulfoxide. After 15 min, a solution of 301.8 mg (1.05 mmol) of the alcohol **21** in 6.0 mL of dichloromethane was added to the reaction mixture over 2 min. After 26 min, 1.1 mL (7.89) of triethylamine was added, and then the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with 50 mL of ether and 20 mL of saturated aqueous $NaHCO_3$. The phases were separated, and the aqueous phase was extracted with two portions of 50 mL of ether. The combined organics were dried ($MgSO_4$) and concentrated under reduced pressure to afford the desired crude aldehyde: R_f = 0.56 (1:1 petroleum ether/ether); ^1H NMR ($CDCl_3$) δ 0.94 (d, 3 H, CH_3, J = 6.5 Hz), 1.12, 1.21 (2s, 18 H, $(CH_3)_3C$), 2.4–2.5 (m, 1 H, CHC), 3.95 (d, 2 H, CH_2O, J = 6.5 Hz), 5.02 (d, 1 H, HCO, J = 3.5 Hz), 9.53 (s, 1 H, HC=O).

(2*R*,3*R*)-1,3-Dihydroxy-2-methyl-4-pentene Dipivaloate (22). To a stirred solution of 301 mg (1.21 mmol) of Tebbe's reagent in 2.5 mL of benzene at 5 °C were added a solution of the above crude aldehyde (roughly 1 mmol) in 2.5 mL of benzene and also 0.10 mL (1.23 mmol) of pyridine. After 20 min, 0.35 mL of 15% aqueous NaOH was added to the reaction mixture. After 15 min, the reaction mixture was diluted with 50 mL of petroleum ether, dried (Na_2SO_4), and filtered through a pad of dry Celite. The solvent was removed under reduced pressure, and the residue was diluted with 50 mL of petroleum ether and filtered through a pad of dry Celite. After the solvent was removed, the residue

was chromatographed on 50 g of florisil with 98:2 petroleum ether/ether to afford 142.1 mg (47.7% from alcohol **21**) of the olefin **22** as a colorless oil: R_f = 0.67 (1:1 petroleum ether/ether); evaporative distillation 70–72 °C (0.06 mmHg); $[\alpha]^{21}_D$ +11.89° (*c* 1.06, $CHCl_3$); IR ($CHCl_3$) 3010, 2970, 2930, 2895, 2870, 1710, 1480, 1460, 1400, 1370, 1285, 1160, 1035, 995, 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, 3 H, CH_3, J = 6 Hz), 1.15 (s, 18 H, $(CH_3)_3C$), 2.1–2.2 (m, 1 H, CHC), 3.82 (abx, 1 H, CHH, J = 12, 2 Hz), 4.04 (abx, 1 H, CHH, J = 12, 3 Hz), 5.1–5.2 (m, 1 H, HCO), 5.2–5.3 (m, 2 H, H_2C=C), 5.7–5.8 (m, 1 H, HC=C). Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.48; H, 9.76.

(2ξ)-4-Deoxy-4-methyl-D-*threo*-pentitol 3,5-Dipivaloate (23). To a stirred solution of 109.5 mg (0.38 mmol) of the olefin **22** in 7.5 mL of acetone and 3.0 mL of water were added 69.9 mg (0.52 mmol) of *N*-methylmorpholine *N*-oxide and 0.39 mL (0.38 mmol) of a 2.5% solution of OsO_4 in *tert*-butyl alcohol. After 10.5 h, the reaction mixture was diluted with 15 mL of water and 1 g of Celite, and then 200 mg of sodium hydrosulfite was added. After 20 min, the reaction mixture was filtered through a wet Celite pad and acidified to pH 1.5. The solution was extracted with three portions of 150 mL of ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. The residue was chromatographed on 10 g of silica gel with ether to afford 110.9 mg (90.5%) of the diol **23** as a mixture of diastereomers: R_f = major 0.08, minor 0.06 (1:1 petroleum ether/ether); evaporative distillation 135–140 °C (0.05 mmHg); IR ($CHCl_3$) 3690, 3540 (br), 2970, 2930, 2870, 1715, 1480, 1460, 1400, 1290, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, 3 H, CH_3, J = 6.8 Hz), 1.18, 1.19 (2s, 18 H, $(CH_3)_3C$), 2.5–2.6 (m, 2 H, CHC, OH), 2.7–2.8 (m, 1 H, OH), 3.4–3.5 (m, 1 H, CHOH), 3.5–3.6 (m, 2 H, CH_2OH), 3.85 (abx, 1 H, HCHOC=O, J = 11, 9 Hz), 3.91 (abx, 1 H, HCHOC=O, J = 11, 6.6 Hz), 4.87 (dd, 1 H, HCOC=O, J = 9.2, 2.4 Hz). Anal. Calcd for $C_{16}H_{30}O_6$: C, 60.35; H, 9.50. Found: C, 60.46; H, 9.46.

(8ξ)-(2*R*,3*S*,5*E*,9*R*)-8-[(Benzyloxy)methyl]-9-(*tert*-butyldimethylsiloxy)-1,3-dihydroxy-2,6-dimethyl-5-decene-4,7-dione Dipivaloate (24). To a stirred solution of 1.43 mL (16.39 mmol) of oxalyl chloride in 65 mL of dichloromethane at 78 °C was added 1.34 mL (18.88 mmol) of dimethyl sulfoxide. After 15 min, a solution of 2.38 g (7.47 mmol) of the diol **23** in 45 mL of dichloromethane was added to the reaction mixture over 3 min. The reaction mixture was allowed to warm slowly to −30 °C and, after 15 min at that temperature, 5.24 mL (37.60 mmol) of triethylamine was added. After 6.5 min, a solution of 6.8489 g (11.21 mmol) of the α-keto phosphoranylidene **17** in 50 mL of dichloromethane was added over 3.5 min. After 20 min, the reaction mixture was allowed to warm to 0 °C. After 1 h, the reaction mixture was diluted with 1.5 L of ether and 400 mL of saturated aqueous NaCl. The organic phase was separated and dried ($MgSO_4$), and then the solvent was removed under reduced pressure. The residue was flash chromatographed on 250 g of silica gel with 9:1 petroleum ether/ether to afford 2.0099 g (41.6%) of the enedione **24** as a slightly yellow oil. A small portion was further chromatographed at medium pressure on a size A Lobar silica column with 9:1 petroleum ether/ether to afford analytically pure samples of both diastereomers: R_f = major 0.51, minor 0.49 (3:1 petroleum ether/ether); IR ($CHCl_3$) major 3020, 2965, 2925, 2850, 1725, 1665, 1610, 1480, 1460, 1365, 1285, 1255, 1150, 1105, 1035, 1005, 915, 840 cm^{-1}, minor: 3020, 2965, 2925, 2850, 1725, 1665, 1610, 1480, 1460, 1370, 1285, 1150, 1115, 920, 845 cm^{-1}; ^1H NMR ($CDCl_3$) major δ −0.01, 0.02 (2s, 6 H, $Si(CH_3)_2$), 0.82 (s, 9 H, $(CH_3)_3C$), 0.85 (d, 3 H, CH_3C, J = 7.1 Hz), 1.02 (d, 3 H, CH_3COSi, J = 6.5 Hz), 1.19, 1.24 (2s, 18 H, $(CH_3)_3CO$), 2.20 (s, 3 H, CH_3C=C), 2.2–2.3 (m, 1 H, CHCCO), 2.3–2.4 (m, 1 H, CHC=O), 3.5–3.9 (m, 4 H, CH_2O), 3.97 (dq, 1 H, HCOSi, J = 2, 6.5 Hz), 4.36 (ab, 1 H, HCHPh, J = 13 Hz), 4.40 (ab, 1 H, HCHPh, J = 13 Hz), 4.40 (ab, 1 H, HCHPh, J = 13 Hz), 5.19 (d, 1 H, CHOC=O, J = 4.0 Hz), 6.83 (s, 1 H, HC=C), 7.2–7.4 (m, 5 H, PhH); minor δ −0.07, −0.01 (2s, 6 H, $(CH_3)_2$), 0.77 (s, 9 H, $(CH_3)_3CSi$), 0.84 (d, 3 H, CH_3C, J = 6.7 Hz), 1.13 (d, 3 H, CH_3CO, J = 6.3 Hz), 1.19, 1.26 (2s, 18 H, $(CH_3)_3C$), 2.0–2.1 (m, 1 H, CHCO), 2.22 (s, 3 H, CH_3C=C), 2.28 (ddd, 1 H, CHC=O, J = 12.0, 6.5, 2.5 Hz), 3.4–3.6 (m, 2 H, CH_2OBn), 3.94 (d, 2 H, CH_2OC=O, J = 7 Hz), 4.02 (dq, 1 H, CHOSi, J = 6.3, 12 Hz), 4.40 (s, 2 H, CH_2Ph), 5.22 (d, 1 H, CHOC=O, J = 4.0 Hz), 6.85 (s, 1 H, HC=C), 7.2–7.4 (m, 5 H, PhH). Anal. Calcd for $C_{36}H_{58}O_8Si$: (M + H)$^+$, 647.3979. Found: (M + H)$^+$, major, 647.3969; minor, 647.3949.

(6ξ,8ξ)-6,9-Anhydro-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-4,7-decodiulose Dipivaloate (25). To a stirred solution of 1.0 g (1.70 mmol) of the enedione **24** in 46 mL of 1:1 acetone/dichloromethane were added 1.99 g (21.23 mmol) of lithium tetrafluoroborate and 0.67 g of *p*-toluenesulfonic acid. After 12 h, the reaction mixture was diluted with 300 mL of ether and 75 mL of saturated aqueous NaCl slightly acidified with 10% aqueous HCl. The phases were separated, and the aqueous phase was washed with 300 mL of ether. The combined organics were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was chromatographed on 100 g of silica gel with 4:1 petroleum ether/ether to afford 588.2 mg (71.4%) of the furanone **25** as a colorless oil: R_f = 0.43 (1:1 petroleum ether/ether); IR ($CHCl_3$) 2970, 2925, 2865, 1755, 1725, 1480, 1455, 1370, 1285, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 0.84, 0.87 (2d, 3 H, CH_3CCO, J = 7.1 Hz, J' = 6.8 Hz), 1.17, 1.21 (2s, 18 H, $(CH_3)_3C$), 1.23, 1.25 (2s, 3 H, CH_3), 1.34, 1.43 (2d, 3 H, CH_3CO, J = 6.6 Hz, J' = 6.1 Hz), 2.4–2.6 (m, 2 H, CHC), 2.78 (ab, 0.5 H, HCHO=O, J = 17.6 Hz), 2.90 (s, 1 H, CH_2C=O), 2.94 (ab, 0.5 H, HCHC=O, J = 17.6 Hz), 3.68 (abx, 0.5 H, HCHOBn, J = 9.7, 3.3 Hz), 3.73 (abx, 0.5 H, HCHOBn, J = 9.7, 6.6 Hz), 3.88 (d, 2 H, CH_2OC=O, J = 8.3 Hz), 3.91 (abx, 0.5 H, HCHOBn, J = 9.5, 2.1 Hz), 3.93 (abx, 0.5 H, HCHOBn, J = 9.5, 4.0 Hz), 4.27 (dq, 0.5 H, $OCHCH_3$, J = 9.4, 6.1 Hz), 4.46, 4.52 (2s, 2 H, CH_2Ph), 4.60 (dq, 0.5 H, $OCHCH_3$, J = 8.3, 6.6 Hz), 5.12 (d, 0.5 H, HCOC=O, J = 2.9 Hz), 5.16 (d, 0.5 H, HCOC=O, J = 2.7 Hz), 7.2–7.4 (m, 5 H, PhH). Anal. Calcd for $C_{30}H_{44}O_6$: (M + H)$^+$, 533.3114. Found: (M + H)$^+$, 533.3133.

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decitol. To a stirred solution of 99.4 mg (0.1866 mmol) of the furanone **25** in 1.8 mL of THF at −78 °C was added 0.36 mL of 1.6 M lithium tetrahydridoaluminate. After 1 h, the reaction mixture was allowed to warm to room temperature. After 4 h total, the reaction mixture was treated sequentially with 18 μL of water, 18 μL of 15% aqueous NaOH, and 54 μL of water. After 0.5 h, the resultant slurry was diluted with THF and filtered through a Celite pad. The solvent was removed under reduced pressure to afford 75.8 mg (100+%) of the crude tetraol as a colorless oil, which was not further purified: R_f = 0.14 (EtOAc); IR ($CHCl_3$) 3450 (br), 3005, 2990, 2940, 2880, 1455, 1380, 1245, 1075, 1040, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (d, 3 H, CH_3CC, J = 7 Hz), 1.2–1.3 (m, 6 H, CH_3), 1.7–1.9 (m, 2 H, CCH_2C), 2.0–2.2 (m, 2 H, CHC), 2.6–2.9 (m, 4 H, OH), 3.4–4.1 (m, 8 H, CH_2O, CHO), 4.52 (s, 2 H, CH_2Ph), 7.28 (s, 5 H, PhH).

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-1,3-*O*-benzylidene-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decitol (26). To a stirred solution of 55.6 mg (0.15 mmol) of the above tetrol in 1 mL of benzene were added 20 μL (0.20 mmol) of benzaldehyde and 2.0 mg (0.01 mmol) of *p*-toluenesulfonic acid. After 22 h, the reaction mixture was directly chromatographed on 10 g of silica gel with 3:2 ether/petroleum ether affording 38.7 mg (56.2%) of the monobenzylidene acetal **26** as a colorless oil: R_f = 0.65 (ether); evaporative distillation 230 °C (0.03 mmHg); IR ($CHCl_3$) 3460 (br), 3010, 3000, 2960, 2890, 1475, 1260, 1120, 1055, 1040, 1015, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–1.4 (m, 9 H, CH_3), 1.5–2.4 (m, 6 H, OH, CCH_2C, CHC), 3.5–4.2 (m, 8 H, CH_2O, CHO), 4.45 (s, 2 H, CH_2Ph), 5.42 (s, 1 H, CHPh), 7.2–7.5 (m, 10 H, PhH). Anal. Calcd for $C_{27}H_{36}O_6$: C, 71.03; H, 7.95. Found: C, 71.03; H, 8.09.

(6ξ,8ξ)-6,9-Anhydro-1,3-*O*-benzylidene-8-[(benzyloxy)-methyl]-2,5,8,10-tetradeoxy-2-*C*-methyl-D-*glycero*-D-*threo*-4,7-decodiulose (27). To a stirred solution of 10 μL (0.1146 mmol) of oxalyl chloride in 400 μL of dichloromethane at −78 °C was added 10 μL (0.1409 mmol) of dimethyl sulfoxide. After 10 min, a solution of 12.4 mg (0.0272 mmol) of the diol **26** in 400 μL of dichloromethane was added to the reaction mixture over 1.0 min. After 19 min, the reaction mixture was treated with 40 μL (0.2870 mmol) of triethylamine, allowed to warm to room temperature, and then diluted with 50 mL of ether and 2 mL of 1 N aqueous HCl. The phases were separated, and the organic phase was extracted with 4 mL of saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue on 1 g of silica gel with

1:1 petroleum ether/ether afforded 10.0 mg (81.3%) of the diketone **27** as a colorless oil: R_f = 0.31 (1:1 petroleum ether/ether); evaporative distillation 240–245 °C (0.03 mmHg); IR ($CHCl_3$) 3005, 2980, 2940, 2860, 1760, 1725, 1455, 1390, 1365, 1240, 1165, 1110, 1040, 1030, 1005, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07, 1.16 (2d, 3 H, CH_3CC, $J = J' = 7.0$ Hz), 1.24 (s, 3 H, CH_3), 1.38, 1.43 (2d, 3 H, CH_3CO, $J = 6.3$ Hz, $J' = 5.6$ Hz), 2.0–2.1 (m, 1 H, CHC), 2.6–2.7 (m, 1 H, CHCO), 2.92, 2.98 (2ab, 1 H, HCHC=O, $J = 18.4$ Hz, $J' = 17.8$ Hz), 3.28, 3.32 (2ab, 1 H, HCHC=O, $J = 17.8$ Hz, $J' = 18.4$ Hz), 3.6–4.4 (m, 6 H, CH_2O, CHO), 4.54 (s, 2 H, CH_2Ph), 5.47 (s, 1 H, CHPh), 7.2–7.6 (m, 10 H, PhH). Anal. Calcd for $C_{27}H_{32}O_6$: C, 71.66; H, 7.13. Found: C, 71.55; H, 7.22.

(6ξ,8ξ)-6,9-Anhydro-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-4,7-decodiulo-1,4-furano-3,7-pyranose (28). To a stirred solution of 6.9 mg (0.0153 mmol) of the diketone **27** in 0.15 mL of THF was added 0.05 mL of 10% aqueous HCl. After 5.5 h, the reaction mixture was diluted with 50 mL of ethyl acetate and solid K_2CO_3 was added to neutralize the acid. The solution was filtered, and the solvent was removed under reduced pressure. The residue was chromatographed on 1 g of silica gel with 2:1 ether/petroleum ether to afford 4.0 mg (72.0%) of the bis(hemiacetal) **28** as a colorless oil: R_f = 0.26 (ether); evaporative distillation 160–165 °C (0.02 mmHg); IR ($CHCl_3$) 3540, 3005, 2970, 2940, 2880, 1450, 1380, 1135, 1105, 1060, 1005, 960, 905, 815, 690; ^1H NMR ($CDCl_3$) δ 1.05, 1.13 (2d, 3 H, CH_3CC, $J = J' = 6.8$ Hz), 1.23, 1.28 (2s, 3 H, CH_3), 1.33, 1.49 (2d, 3 H, Ch_3CO, $J = 3.9$ Hz, $J' = 6.1$ Hz), 2.0–2.4 (m, 6 H, CHC, Ch_2C, OH), 3.3–4.1 (m, 6 H, CH_2O, CHO), 4.48, 4.50 (2ab, 1 H, HCHPh, $J = 11.9$ Hz, $J' = 12.4$ Hz), 4.57, 4.58 (ab, 1 H, HCHPh, $J = 12.4$ Hz, $J' = 11.9$ Hz), 7.2–7.5 (m, 5 H, PhH). Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.92; H, 7.74. Found: C, 66.15; H, 7.87.

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-7-*O*-benzyl-1,3-*O*-benzylidene-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-8-*C*-methyl-D-*glycero*-D-*threo*-decitol. To a stirred solution of 11.2 mg (0.0245 mmol) of the diol **26** in 0.10 mL of *N,N*-dimethylformamide were added 9.5 mg (0.0620 mmol) of barium oxide, 2.5 mg (0.0146 mmol) of barium hydroxide, and 3.6 μL (0.0303 mmol) of benzyl bromide. After 0.5 h at room temperature, the reaction mixture was warmed to 40 °C. After 22 h, to the reaction mixture were added 7.2 μL (0.0606 mmol) of benzyl bromide, 9.5 mg (0.0620 mmol) of barium oxide, and 2.5 mg (0.0146 mmol) of barium hydroxide. After 12 h more, the reaction mixture was diluted with 50 mL of dichloromethane and 5 mL of saturated aqueous $NaHCO_3$. The phases were separated, and the aqueous phase was extracted with 40 mL of ether. The combined organics were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on 1 g of silica gel with 4:1 petroleum ether/ether and then 1:1 petroleum ether/ether to afford 9.9 mg (73.8%) of monobenzylated product. Further elution afforded 2.6 mg of starting material (96.1% based on unrecovered starting material). The product was a colorless oil: R_f = 0.27 (1:1 ether/petroleum ether); evaporative distillation 240–245 °C (0.02 mmHg); IR ($CHCl_3$) 3460, 3005, 2970, 2930, 2860, 1450, 1385, 1360, 1240, 1110, 1030, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H, CH_3, CH_3CC), 1.15 (s, 3 H, CH_3), 1.19 (d, 3 H, CH_3CO, $J = 7$ Hz), 1.4–2.2 (m, 5 H, CCH_2C, CCHC, OH), 3.4–4.1 (m, 8 H, CH_2O, CHO), 4.33 (ab, 1 H, HCHPh, $J = 12$ Hz), 4.36 (ab, 1 H, HCHPh, $J = 6$ Hz), 4.49 (ab, 1 H, HCHPh, $J = 6$ Hz), 4.54 (ab, 1 H, HCHPh, $J = 12$ Hz), 5.47 (s, 1 H, CHPh), 7.2–7.5 (m, 15 H, PhH). Anal. Calcd for $C_{34}H_{42}O_6$: C, 74.70; H, 7.74. Found: C, 74.87; H, 7.80.

(6ξ,7ξ,8ξ)-6,9-Anhydro-7-*O*-benzyl-1,3-*O*-benzylidene-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-8-*C*-methyl-D-*glycero*-D-*threo*-4,7-deco-4-ulose. To a stirred solution of 10 μL (0.1146 mmol) of oxalyl chloride in 0.40 mL of dichloromethane at −78 °C was added 10 μL (0.1409 mmol) of dimethyl sulfoxide. After 15 min, a solution of 3.5 mg (0.0064 mmol) of the above alcohol in 0.40 mL of dichloromethane was added to the reaction mixture over 1 min. After 22 min, the reaction mixture was treated with 40 μL (0.2870 mmol) of triethylamine, allowed to warm to room temperature, and then diluted with 50 mL of ether and 6 mL of 10% aqueous HCl. The phases were separated, and the organic phase was extracted with 10 mL of saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue on 1 g of silica gel with 4:1 petroleum ether/ether afforded 2.6 mg (74.6%) of the acyclic ketone as a colorless lil: R_f 0.36 (1:1 ether/petroleum ether); IR ($CHCl_3$) 3005, 2965, 2860, 1720, 1455, 1390, 1360, 1115, 1040, 1030, 1010, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 0.97, 1.08 (2d, 3 H, CH_3CC, $J = J' = 7.0$ Hz), 1.23 (s, 3 H, CH_3), 1.24, 1.29 (2d, 3 H, CH_3CO, $J = J' = 6.2$ Hz), 1.9–2.2 (m, 2 H, CHC), 2.66 (ab, 1 H, HCHC=O, $J = 17.0$ Hz), 2.99 (ab, 1 H, HCHC=O, $J = 17.0$ Hz), 3.39 (abx, 1 H, HCHOCO, $J = 9.8$, 5.4 Hz), 3.44 (abx, 1 H, HCHOCO, $J = 9.8$, 4.3 Hz), 3.82, 3.85 (2d, 1 H, CHOBn, $J = 6.2$ Hz, $J' = 6.0$ Hz), 3.99 (abx, 0.66 H, HCHOBn, $J = 12.5$, 1.4 Hz), 4.00 (d, 0.66 H, CH_2OBn, $J = 6.7$ Hz), 4.04 (abx, 0.66 H, HCHOBn, $J = 12.5$, 2.5 Hz), 4.20 (d, 1 H, CHC=O, $J = 2.7$ Hz), 4.2–4.3 (m, 1 H, CHOC), 4.33 (ab, 1 H, HCHPh, $J = 11.9$ Hz), 4.38 (ab, 1 H, HCHPh, $J = 11.9$ Hz), 4.52 (ab, 1 H, HCHPh, $J = 12.1$ Hz), 4.63 (ab, 1 H, HCHPh, $J = 12.1$ Hz), 7.2–7.6 (m, 15 H, PhH). Anal. Calcd for $C_{34}H_{40}O_6$: $(M + H)^+$, 545.2905. Found: $(M + H)^+$, 545.2880.

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-7-*O*-benzyl-1,3-*O*-benzylidene-8-[(benzyloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-4,7-decitol Pivaloate (29). To a stirred solution of 19.1 mg (0.0349 mmol) of the above alcohol in 0.20 mL of dichloromethane were added 8.6 μL (0.0713 mmol) of pivaloyl chloride and 12.8 mg (0.1048 mmol) of *N',N'*-dimethylaminopyridine. After 20 h, a further 4.3 μL (0.356 mmol) of pivaloyl chloride and 6.4 mg (0.0524 mmol) of *N',N'*-dimethylaminopyridine were added. After 8 h, the reaction was diluted with 120 mL of ether and 5 mL of 10% aqueous HCl. The phases were separated, and the organic phase was extracted with 10 mL of saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography on 5 g of silica gel with 2:1 petroleum ether/ether afforded 16.4 mg (74.5%) of the desired ester **29** as a colorless oil: R_f = 0.54 (1:1 petroleum ether/ether); IR ($CHCl_3$) 2980, 2940, 2870, 1730, 1460, 1380, 1295, 1175, 1120, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–1.3 (m, 18 H, CH_3), 1.6–2.2 (m, 4 H, CCHC, CCH_2C), 3.4–4.1 (m, 7 H, CH_2O, CHO), 4.40 (ab, 1 H, HCHPh, $J = 12$ Hz), 4.44 (s, 2 H, CH_2Ph), 4.50 (ab, 1 H, HCHPh), $J = 12$ Hz), 5.26 (dt, 1 H, HCOC=O, $J = 1.5$, 8 Hz), 5.49 (s, 1 H, HCPh), 7.2–7.5 (m, 15 H, PhH). Anal. Calcd for $C_{39}H_{50}O_7$: C, 74.26; H, 7.99. Found: C, 74.34; H, 7.99.

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-7-*O*-benzyl-8-[(benzyloxy)-methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decitol Pivaloate. To a stirred solution of 54.2 mg (0.0859 mmol) of the ester **29** in 0.75 mL of THF at 50 °C was added 0.25 mL of 10% aqueous HCl. After 26 h, the reaction was diluted with 100 mL of ether and 10 mL of 2% aqueous HCl. The phases were separated, and the aqueous phase was extracted with 100 mL of ether. The combined organics were diluted with 150 mL of petroleum ether and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford the crude diol, which was not pufiried but used directly in the next reaction: R_f = 0.07 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3400 (br), 3005, 2985, 2950, 2880, 1725, 1480, 1455, 1400, 1375, 1280, 1160, 1105, 1030, 970, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 200 MHz δ 0.85, 0.91 (2d, 3 H, CH_3CC, $J = J' = 7.1$ Hz), 1.15 (s, 9 H, $(CH_3)_3C$), 1.1–1.3 (m, 6 H, CH_3C), 1.6–2.1 (m, 4 H, CCH_2C, CCHC), 2.6–3.1 (br, s, 2 H, OH), 3.3–4.1 (m, 7 H, CH_2O, CHO), 4.2–4.4 (m, 4 H, CH_2Ph), 4.8–5.0 (m, 1 H, HCOC=O), 7.2–7.4 (m, 10 H, PhH).

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-7-*O*-benzyl-8-[(benzyloxy)-methyl]-2,5,8,10-tetradeoxy-1,3-*O*-isopropylidene-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decitol Pivaloate. To a stirred solution of the above crude diol in 0.80 mL of acetone were added 0.10 mL (0.813 mmol) of dimethoxypropane and 0.10 mL of a 0.1 M solution of *p*-toluenesulfonic acid in THF. After 6 h, the reaction mixture was diluted with 100 mL of ether and 5 mL of saturated aqueous $NaHCO_3$. The phases were separated, and the organic phase was dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was chromatographed on 5 g of silica gel with 4:1 petroleum ether/ether to afford 31.8 mg (70%) of the desired acetonide as a colorless oil: R_f = 0.59 (1:1 ether/petroleum ether); IR ($CHCl_3$) 3010, 2990, 2950, 2880, 1730, 1490, 1450, 1385, 1360, 1280, 1240, 1150, 1110, 1040, 1020, 940, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 200 MHz δ 1.09 (d, 3 H, CH_3CC, $J = 7.2$ Hz), 1.15 (s, 9 H, $(CH_3)_3C$), 1.1–1.4 (m, 12 H, Ch_3), 1.6–2.1 (m, 4 H, CCH_2C, CCHC), 3.2–4.1 (m, 7 H, CH_2O, CHO), 4.4–4.6 (m, 4 H, CH_2Ph), 5.09 (dt, 1 H, CHOC=O, $J = 1.5$, 8.0 Hz), 7.2–7.4

(m, 10 H, PhH). Anal. Calcd for $C_{35}H_{50}O_7$: C, 72.13; H, 8.65. Found: C, 72.19; H, 8.71.

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-2,5,8,10-tetradeoxy-8-(hydroxymethyl)-1,3-*O*-isopropylidene-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decitol 4-Pivaloate (30). To a stirred solution of 28.7 mg (0.0492 mmol) of the above ester in 2.0 mL of ethyl acetate were added 10 mL of acetic acid and 20 mg of 10% palladium on carbon. The reaction mixture was stirred vigorously under a hydrogen atmosphere for 7 h. The catalyst was removed by filtration, and the solvent was removed under reduced pressure. The residue was chromatographed on 1 g of silica gel with ether to afford 17.9 mg (90.4%) of the diol **30** as a colorless oil: R_f = 0.14 (ether); evaporative distillation 170 °C (0.03 Torr); IR ($CHCl_3$) 3500 (br), 2980, 2940, 2880, 1730, 1480, 1460, 1385, 1280, 1165, 1080, 1035, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) 200 MHz δ 0.84 (d, 3 H, CH_3CC, J = 7.0 Hz), 1.02 (d, 3 H, Ch_3CO, J = 6.4 Hz), 1.2–1.6 (m, 18 H, CH_3), 1.9–2.4 (m, 6 H, CCH_2C, CCHC, OH), 3.3–4.4 (m, 7 H, CH_2O, CHO), 5.10 (apparent t, 1 H, CHOC=O, J = 8 Hz). Anal. Calcd for $C_{21}H_{38}O_7$: C, 62.66; H, 9.52. Found: C, 62.56; H, 9.55.

(4ξ,6ξ,7ξ,8ξ)-6,9-Anhydro-8-[(*tert*-butyldiphenylsiloxy)methyl]-2,5,8,10-tetradeoxy-1,3-*O*-isopropylidene-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decitol 4-Pivaloate. To a stirred solution of 13.6 mg (0.0338 mmol) of **30** in 0.50 mL of dichloromethane were added 17.6 μL (0.0676 mmol) of *tert*-butylchlorodiphenylsilane and 14.5 mg (0.1183 mmol) of *N',N'*-dimethylaminopyridine. After 2.25 h, the reaction mixture was diluted with 100 mL of ether and 4 mL of 10% aqueous HCl. The phases were separated, and the organic phase was extracted with 8 mL of saturated aqueous $NaHCO_3$ and then dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was chromatographed on 1 g of silica gel with 4:1 petroleum ether/ether to afford 19.8 mg (91.4%) of the desired silyl ether as a colorless oil: R_f = 0.40 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3500, 3000, 2980, 2940, 2870, 1730, 1460, 1430, 1380, 1280, 1160, 1110, 1000, 820, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 200 MHz δ 0.73 (d, 3 H, CCH_3C, J = 7.0 Hz), 0.9–1.5 (m, 30 H, CH_3), 1.7–2.1 (m, 4 H, CCH_2C, CCHC), 1.80 (br s, 1 H, OH), 3.3–4.4 (m, 7 H, CH_2O, CHO), 4.96 (apparent t, 1 H, CHOC=O, J = 8 Hz), 7.3–7.7 (m, 10 H, PhH). Anal. Calcd for $C_{37}H_{56}O_7Si$: C, 69.34; H, 8.81. Found: C, 69.27; H, 8.97.

(4ξ,6ξ,8ξ)-6,9-Anhydro-8-[(*tert*-butyldiphenylsiloxy)methyl]-2,5,8,10-tetradeoxy-1,3-*O*-isopropylidene-2-methyl-6-*C*-methyl-D-*glycero*-D-*threo*-decoulose Pivaloate (31). To a stirred solution of 10 μL (0.1146 mmol) of oxalyl chloride in 0.40 mL of dichloromethane at −78 °C was added 10 μL (0.1409 mmol) of dimethyl sulfoxide. After 10 min, a solution of 13.8 mg (0.0215 mmol) of the above alcohol in 0.40 mL of dichloromethane was added to the reaction mixture over 1.5 min. After 20 min, the reaction mixture was treated with 40 μL (0.2870 mmol) of triethylamine, allowed to warm to room temperature, and then diluted with 100 mL of ether and 4 mL of 10% aqueous HCl. The phases were separated, and the organic phase was extracted with 8 mL of saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue on 1 g of silica gel with 9:1 petroleum ether/ether afforded 13.3 mg (96.7%) of the ketone **31** as a colorless oil: R_f = 0.55 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3000, 2980, 2940, 2870, 1760, 1730, 1480, 1460, 1425, 1380, 1280, 1160, 1110, 1005, 830, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 200 M Hz δ 0.71, 0.83 (2d, 3 H, CH_3CC, J = J' = 6.5 Hz), 1.00 (s, 9 H, $(CH_3)_3CSi$), 1.09 (d, 3 H, CH_3CO, J = 6.1 Hz), 1.16 (s, 9 H, $(CH_3)_3CCO$), 1.22, 1.30 (2s, 6 H, $(CH_3)_2C$), 1.37, 1.40 (2 H, 3 H, CH_3), 1.9–2.4 (m, 4 H, CCH_2C, CCHC), 3.2–4.4 (m, 6 H, CH_2O, CHO), 5.08 (m, 1 H, CHOC=O), 7.3–7.7 (m, 10 H, PhH). Anal. Calcd for $C_{37}H_{54}O_7Si$: $(M + H)^+$, 639.3717. Found: $(M + H)^+$, 639.3705.

1,7:6,9-Dianhydro-8-[(*tert*-butyldiphenylsiloxy)methyl]-2,5,8,10-tetradeoxy-2-methyl-6-*C*-methyl-α-D-*threo*-D-*ido*-7-decoulo-7,3-pyranose Pivaloate (32). To a stirred solution of 10.1 mg of the ketone **31** in 0.5 mL of THF was added 0.17 mL of 10% aqueous HCl. After 1 h, the reaction mixture was diluted with 50 mL of ether and 6 mL of 3% aqueous HCl. The phases were separated, and the aqueous phase was extracted with 50 mL of ether. The combined organics were diluted with 75 mL of petroleum ether and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was chromatographed on 1 g of silica gel with a solvent gradient starting with 3:1 petroleum ether/ether and ending with ether to afford 3.3 mg (35.9%) of the ketal **32** as a colorless oil: R_f = 0.24 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3000, 2980, 2870, 1730, 1460, 1380, 1280, 1140, 1110, 1080, 1050, 1030, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 0.89 (d, 3 H, CH_3CC, J = 7.1 Hz), 1.02 (d, 3 H, CH_3CO, J = 6.1 Hz), 1.05 (s, 9 H, $(CH_3)_3CSi$), 1.15 (s, 9H, $(CH_3)CC$=O), 1.22 (s, 3 H, CH_3), 1.89 (dddq, 1 H, CH_3CHC, J = 1.8, 4.9, 6.6, 7.1 Hz), 2.22 (dd, 1 H, HCHCO, J = 13.4, 4.6 Hz), 2.31 (dd, 1 H, HCHCO, J = 13.4, 10.3 Hz), 2.32 (dt, 1 H, J = 10.0, 6.4 Hz), 3.56 (dq, 1 H, CHO, J = 10.0, 6.1 Hz), 3.60 (dd, 1 H, HCHO, J = 9.8, 4.9 Hz), 3.66 (d, 2 H, CH_2OSi, J = 6.4 Hz), 4.03 (dd, 1 H, $OCHCHCH_3$, J = 10.3, 1.8 Hz), 4.09 (dd, 1 H, HCHO, J = 9.8, 6.6 Hz), 4.89 (dt, 1 H, CHOC=O, J = 4.6, 10.3 Hz), 7.4–7.5 (m, 6 H, *p*-, *m*-PhH), 7.6–7.7 (m, 4 H, *O*-PhH); irradiation at 0.89 collapses 1.89 to a ddd; irradiation at 1.02 collapses 3.56 to a d; irradiation at 4.89 collapses 2.22 to a d, 2.31 to a d, and 4.09 to a d; NOE difference with irradiation at 1.22 enhances d at 0.89, dd at 2.22, and dt at 2.32; NOE difference with irradiation at 0.89 enhances s at 1.22. Anal. Calcd for $C_{34}H_{48}O_6Si$: $(M + H)^+$, 581.3298. Found: $(M + H)^+$, 581.3294. Further elution afforded 2.3 mg (24.3%) of a hemiketal: R_f = 0.17 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3350, 2970, 2940, 2890, 2830, 1725, 1460, 1430, 1390, 1360, 1260, 1170, 1110, 1080, 1050, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 0.88 (d, 3 H, CH_3CC, J = 6.8 Hz), 1.04 (s, 9 H, $(CH_3)_3CSi$), 1.05 (d, 3 H, CH_3CO, J = 6.0 Hz), 1.19 (s, 9 H, $(CH_3)_3C$), 1.34 (s, 3 H, CH_3), 1.88 (dd, 1 H, HCHC, J = 13.4, 6.8 Hz), 2.13 (dd, 1 H, HCHC, J = 13.4, 7.3 Hz), 2.16 (ddd, 1 H, CHCO, J = 11.0, 10.5, 5.0 Hz), 2.2–2.3 (m, 1 H, $CHCH_3$), 3.0–3.1 (m, 3 H, CH_2OH), 3.54 (dq, 1 H, CHO, J = 10.5, 6.0 Hz), 3.61 (dd, 1 H, HCHOSi, J = 11.0, 9.5 Hz), 4.03 (dd, 1 H, HCHOSi, J = 9.5, 5.0 Hz), 4.23 (s, 1 H, OCOH), 4.44 (ddd, 1 H, CHOCO, J = 8.5, 7.3, 6.8 Hz), 5.03 (dd, 1 H, CHO, J = 8.5, 2.2 Hz), 7.3–7.7 (m, 10 H, PhH); irradiation at 1.05 collapses 3.54 to a d; irradiation at 4.03 collapses 3.61 to a d and 2.16 to a dd; irradiation at 4.44 collapses 1.88 to a d, 2.13 to a d, and 5.03 to a d; irradiation at 5.03 collapses 4.44 to a d and 2.2–2.3 m; NOE difference with irradiation at 1.34 gave no definite enhancements. Anal. Calcd for $C_{34}H_{50}O_7Si$: $(M + H)^+$, 581.3298. Found: $(M + H)^+$, 581.3311. Further elution afforded 2.9 mg (30.6%) of a mixture of two additional compounds that were converted to a single compound by treatment with 0.1 N *p*-toluenesulfonic acid in $CHCl_3$. This material was again chromatographed on 0.5 g of silica gel with 2:1 petroleum ether/ether to afford 2.7 mg of a colorless oil: R_f = 0.16 (1:1 petroleum ether/ether); IR ($CHCl_3$) 3500, 2970, 2940, 2860, 1725, 1470, 1430, 1400, 1290, 1170, 1120, 1030, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 1.02 (d, 3 H, CH_3CC, J = 7.1 Hz), 1.04 (s, 9 H, $(CH_3)_3CSi$), 1.09 (d, 3 H, CH_3CO, J = 5.9 Hz), 1.19 (s, 9 H, $(CH_3)_3CCO$), 1.30 (s, 3 H, CH_3), 2.01 (abx, 1 H, HCHCO, J = 13.2, 8.4 Hz), 2.10 (abx, 1 H, HCHCO, J = 13.2, 6.7 Hz), 2.1–2.2 (m, 1 H, $CHCH_2OSi$), 2.2–2.3 (m, 1 H, $CHCH_3$), 2.94 (br s, 1 H, OH), 3.62 (abx, 1 H, HCH, J = 10.7, 4.9 Hz), 3.72 (dq, 1 H, $OCHCH_3$, J = 5.0, 5.9 Hz) 3.75 (dd, 1 H, CHO, J = 3.2, 6.5 Hz), 3.78 (abx, 1 H, HCH, J = 10.7, 10.0 Hz), 3.87 (abx, 1 H, HCH, J = 11.1, 5.8 Hz), 4.06 (abx, 1 H, HCH, J = 11.1, 6.5 Hz), 4.36 (ddd, 1 H, CHOCO, J = 8.4, 6.7, 3.2 Hz), 5.43 (s, 1 H, COH), 7.3–7.8 (m, 10 H, PhH); irradiation at 1.09 collapses 3.72 to a d; irradiation at 4.36 collapses 3.75 to a d and 2.2–2.3 m; NOE difference with irradiation at 1.30 gave no definite enhancements. Anal. Calcd for $C_{34}H_{50}O_7Si$: $(M + H)^+$, 581.3298. Found: $(M + H)^+$, 581.3289. To a stirred solutions of each of these three products in acetone was added excess Jones reagent. The ketal **32** was not affected, whereas the two hemiketals were both rapidly consumed.