Synthesis of Undeculofuranoside Derivatives of the Herbicidins and of Analogues

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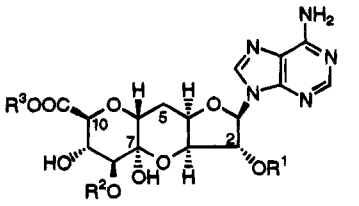
Received February 14, 1995[⊗]

The condensation of 3-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexodialdo-1,4-furanose (obtained in six steps (35%) from D-glucurono-6,3-lactone) with the lithium enolate of (±)-6-*endo*-chloro-5-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]heptan-2-one (derived in six steps (25%) from the Diels–Alder adduct of furan to 1-cyanovinyl acetate) was highly *exo* face selective giving two major aldols that were separated readily. One of them was converted to 6,10-anhydro-5-deoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-α-D-*arabino*-L-*ido*-7-undeculofuranose-(1,4)-pyranose-(7,3), a semiprotected form of the long-chain carbohydrate moiety of the herbicidins. The synthesis implies the acid-promoted isomerization of 10,11-anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-C-[(2-nitrophenyl)selenomethyl]-β-L-*ido*-L-*ido*-undecofuranose.

Introduction

The search for new antibiotics by fermentation technologies has produced unusual nucleosides such as mildiomycin containing a branched decose derivative,[1] the tunicamycins,[2] the streptovirudins,[3] the corynetoxins,[4] hikizimycin,[5] and the herbicidins[6] (**1**) and aureonuclemycin[7] (**2**) that incorporate undecose moieties[8] within their structure. These complex systems have stirred up a great interest among synthetic chemists and some rather imaginative and elegant syntheses have been proposed.[9] The herbicidins exhibit herbicidal and antialgal activity; herbicidin A (**1a**) and B (**1b**), as well as aureonuclemycin (**2**), are efficient inhibitors of *Xanthomonas oryzae*, a bacterium which causes rice infection.[6,7] Their carbohydrate moiety is composed of 6,10-anhydro-5-deoxy-β-D-*arabino*-L-*ido*-7-undeculo-(7,3-pyranose)-furanosiduronic acid, a rare long-chain carbohydrate that has an unusual furano-pyrano-pyran skeleton and which can be viewed as 5-*C*-(α-D-*arabino*-2-hexulopyranosyl)-5-deoxy-D-*xylo*-furanose. A first synthesis of this type of sugar was proposed by Gallagher and co-workers[10] in 1993. Preliminary studies in our group have led to the development of a total synthesis of 6,10-anhydro-5-deoxy-DL-*lyxo*-DL-*talo*-7-undeculofuranuronic acid and derivatives.[11] We report here the further development of our approach to the asymmetric synthesis of an undeculofuranoside derivative that has the same absolute configuration as the carbohydrate portion of the herbicidins (**1**) and aureonuclemycin (**2**).[12]



Herbicidins (**1**)
SI2245 (**1g**)
Aureonuclemycin (**2**)

		R^1	R^2	R^3
1a	A	Me	MeCH=CH(CH_2OH)CO	Me
1b	B	Me	H	Me
1c	C	H	H	Me
1d	E	Me	Me_2CHCO-	Me
1e	F	Me	MeCH=C(Me)CO-	Me
1f	G	H	MeCH=C(Me)CO-	H
1g		Me	MeCO-	Me
2		H	H	H

Retrosynthetic Plan

If one considers the 6,10-anhydro-5-deoxy-7-undeculofuranose (**3**) to be derived from the branched sugar **4**, its *trans*-2,6-tetrahydropyran unit might arise from an intramolecular alcoholysis of the terminal epoxide having

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1995.

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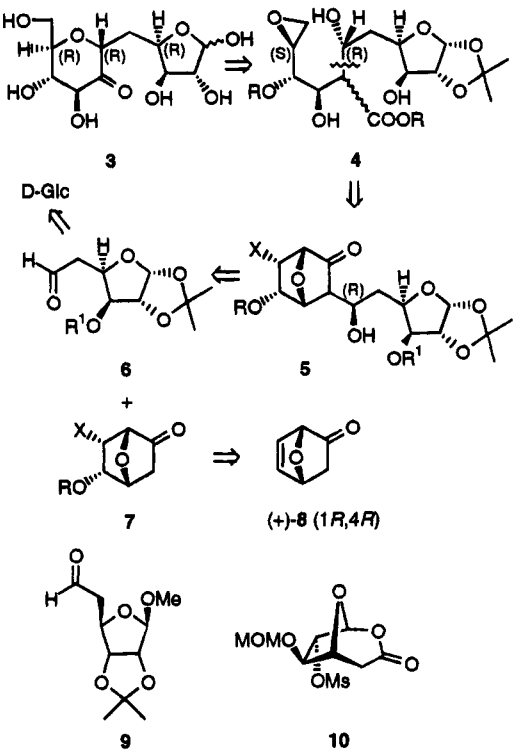
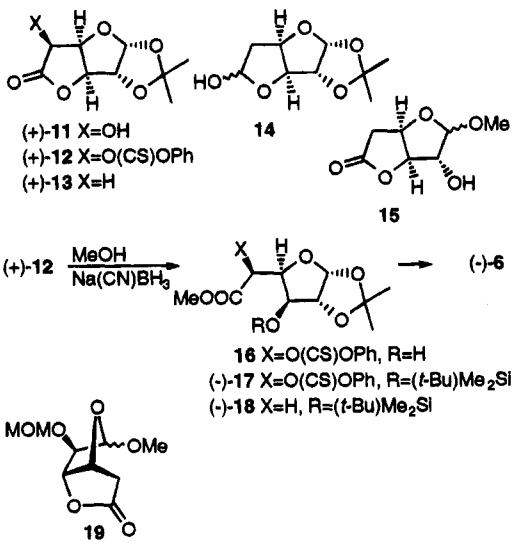
the (10S) configuration. Compound **4** should be the result of the Baeyer–Villiger oxidation of the bicyclic ketone **5** followed by methanolysis and reduction of the intermediate furanose and base-induced 1,3-elimination of the nucleofugal X group (with inversion of configuration at C(10)). Aldol **5** might result from the cross-aldolization of an aldehyde of type **6** (a 5-deoxy-D-glucose derivative) and ketone of type **7**. In order to test the feasibility of this plan we carried out a model study[11] with aldehyde (±)-**9** and uronolactone (±)-**10**, both compounds being readily available from the Diels–Alder adduct of furan to 1-cyanovinyl acetate[13] using methods of the "naked sugar" approach.[14] We then developed an efficient and highly stereoselective method for introducing two different substituents at the *endo* positions C(5) and C(6) of 7-oxabicyclo[2.2.1]heptan-2-one. As will be shown in this report, this has allowed us to generate a bicyclic ketone of type **7** from the racemic enone (±)-**8**. The lithium enolate of (±)-**7** reacted with homochiral aldehyde (−)-**6** (R^1 = (*t*-Bu)Me_2Si) derived from D-glucuronolactone giving a separable mixture of two major aldols with a *syn/anti* selectivity of ca. 1:28. One of them was converted into a protected form of the undeculose of the herbicidins and of analogues.



Results and Discussion

Aldehyde (−)-**6** (R = (*t*-Bu)Me_2Si) was prepared in six steps (35%, overall yield) from commercially available D-glucurono-6,3-lactone via its acetonide (+)-**11**.[15] The unprotected alcoholic moiety was converted into the corresponding phenyl thiocarbonate (+)-**12**.[16,17] Reduction with Bu_3SnH (AIBN, toluene, 80 °C) afforded 5-deoxyuronolactone (+)-**13**, the reduction of which with diisobutylaluminum hydride (DIBAH) provided lactol **14** which refused to undergo cross-aldolizations with 7-oxabicyclo[2.2.1]heptan-2-one derivatives. Attempts to open the lactone moiety of (+)-**13** with MeOH in the presence of K_2CO_3, KCN, or MsOH all failed; methyl furanosides **15** were formed instead. With MeONa/THF only decomposition was observed. Whereas the treatment of (+)-**12** with MeOH/K_2CO_3 (0 °C, 20 min) or with MeOH, KCN (20 °C, 1 h) led to (+)-**11**, methanolysis of (+)-**12** in the presence of Na(CN)BH_3 (1.5 equiv, 0 °C) afforded methyl uronate **16**, the alcoholic moiety of which was silylated with (*t*-Bu)$Me_2SiOSO_2CF_3$/2,6-lutidine to give (−)-**17**. When $NaBH_4$ was used instead of Na(CN)BH_3, a complex mixture of products was formed. The high selectivity of the methanolysis (+)-**12** to yield **16** in the presence of Na(CN)BH_3 remains unexplained for the moment. Radical-induced reduction of (−)-**17** with Bu_3SnH (AIBN, toluene, 80 °C) gave ester (−)-**18**, the reduction of which with DIBAH provided the required synthetic intermediate (−)-**6** (R^1 = (*t*-Bu)Me_2Si).



Treatment of **16** with $CH_2(OMe)_2/CH_2Cl_2$ and P_2O_5 furnished **19**, a compound also obtained as a 1:6.5 mixture of methyl α- and β-furanosides from the racemic epoxy ketone **20**.[18] Baeyer–Villiger oxidation of **20** led to lactone **21**, the methanolysis of which (MeOH, $MeSO_3H$) induced a regiospecific intramolecular epoxide ring opening by the intermediate uronic acid with formation of the γ-lactone **22**. Protection of the alcoholic moiety of **22** as a MOM ether gave (±)-**19**.

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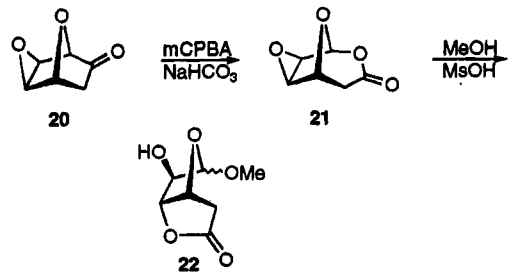


Bicyclic ketones of type **7** must have two different substituents at the *endo* positions of centers C(5) and C(6). Furthermore, X should be a nucleofugal group capable of resisting the strongly basic conditions of cross-aldolizations with lithium enolates. Because of the electron-releasing ability of its carbonyl group,[19,20] enone (+)-**8** gave the single adduct (−)-**23** with PhSeCl. Oxidation with mCPBA usually led to oxidative elimination of selenium with formation of the corresponding chloroolefin. When run at −65 °C, the intermediate selenoxide reacted with Ac_2O/AcONa and underwent a seleno-Pummerer rearrangement[21] without significant elimination of benzeneselenenic acid. This led to a mixture of (−)-**24**, (−)-**25**, and **26** which could be separated and isolated in 60%, 10%, and 7% yield, respectively. The appearance of olefin **26** can be explained in terms of the formation of the (phenylseleno)carbenium ion intermediate **27** which undergoes competitive elimination together with its nucleophilic quenching. A similar observation has been reported by Koizumi and co-workers[22] for the Pummerer rearrangements of 7-oxabicyclo[2.2.1]hept-2-yl sulfoxides. The *endo* configuration of the chloro substituent in (−)-**24** was given by the coupling constants ^3J(H-C(1),H-C(6)) = 6.0 Hz and ^4J(H-C(4),H-C(6)) = 1.8 Hz;[23] the *endo* configuration of the phenylseleno group was confirmed by the observation of NOE's in the ^{1}H-NMR spectrum between the aromatic protons (δ_H = 7.30−7.27 ppm) and H_{endo}-C(3) (δ_H = 2.99 ppm) and H-C(4) (δ_H = 4.33 ppm) signals. Similar observations were made in the ^{1}H-NMR spectrum of (−)-**25**.

Reduction of (−)-**24** with Bu_3SnH (AIBN/toluene, 80 °C) led to a 6:1 mixture (86%) of *endo* (+)-**28** and *exo*-acetate **29**. Saponification, followed by protection of the alcoholic moieties as MOM ethers gave (−)-**30** and **31**, respectively, which could not be separated. In the racemic series (starting with (±)-**8** derived from the Diels−Alder adduct (±)-**32** of furan to 1-cyanovinyl acetate), (±)-**30** could be obtained pure after a single crystallization. Baeyer−Villiger oxidation of (−)-**30** and **31** gave uronolactones (−)-**33** and **34**, respectively, which could be separated by flash chromatography. Their ^{1}H-NMR data confirmed their structures (see Experimental Section). Similarly, reduction of (−)-**25** with Bu_3SnH gave (+)-**35** (63%). Saponification of (+)-**35** followed by

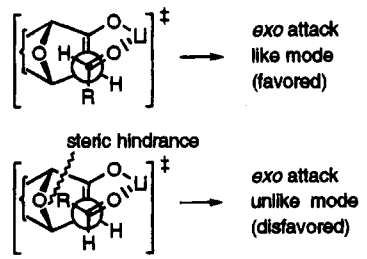
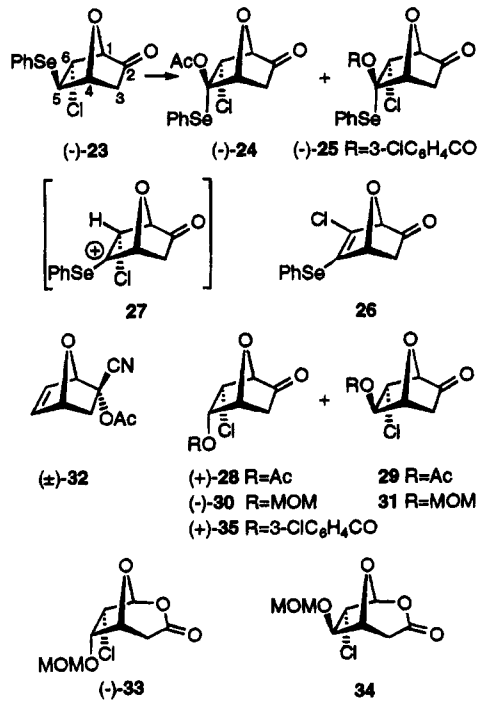


Figure 1. Zimmerman−Traxler model.



treatment with $(MeO)_2CH_2/P_2O_5$ gave (−)-**30** (76%). The formation of the *exo* acetate **29** could not be suppressed by using benzene or chlorobenzene instead of toluene as solvent. With $(Me_3Si)_3SiH$ the reduction of (−)-**24** gave an unknown secondary product (ca. 1/3) together with (+)-**28**. Under conditions identical to those used to convert (−)-**24** into (−)-**30**, compounds (±)-**24** and (±)-**25**, were transformed into crystalline (±)-**30** (25% overall yield in six steps from (±)-**32**).

The condensation of the lithium enolate of (−)-**33** with aldehyde (−)-**6** (THF, −65 °C) led to 4.5:1 mixture (49%) of β-hydroxy lactones (−)-**36** and **37** (together with 28% of unreacted (−)-**33**). Under the same conditions, the condensation of (−)-**6** with the racemic lactone (±)-**33** provided a nonseparable 10:3:6:1 mixture of (+)-**38**, **39**, (−)-**36**, and **37**. We then explored the possibility of running cross-aldolizations of ketone (±)-**30** with (−)-**6**. The lithium enolate of (±)-**30** added to (−)-**6** (THF, −65 °C, 3 h) giving a 16:<1:12:1 mixture of aldols (−)-**40**, **41**, (−)-**42**, **43** (83% yield, 95% of conversion of (±)-**30**). Flash chromatography on silica gel gave two main fractions from which (−)-**40** and (−)-**42** were obtained by crystallization in 36% and 33% yield, respectively. When run at −90 °C, the condensation was no more selective than at −65 °C. Nevertheless, the method realized an optical resolution of the racemic ketone (±)-**30**. As expected for steric reasons,[24] only the *exo* mode of addition of the aldehyde (−)-**6** to the bicyclic enolate was observed. The (3′*S*,6*R*) configuration at C(3′) and C(6) of aldol (−)-**40** was established in the tetrahydropyranyl derivatives **68** and (+)-**69** (see later) and was consistent with that expected from a cyclic structure of the cross-aldolization

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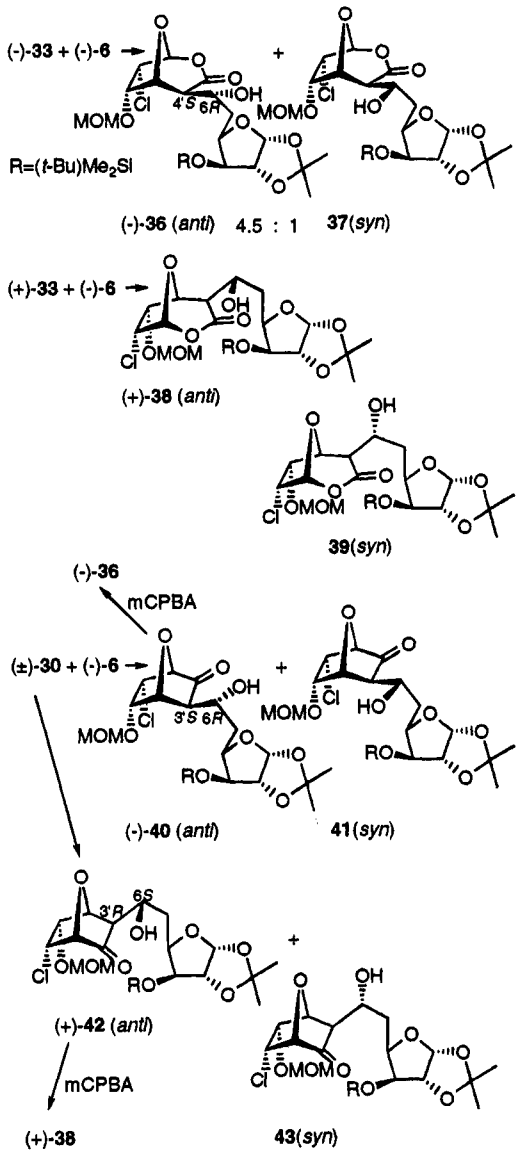
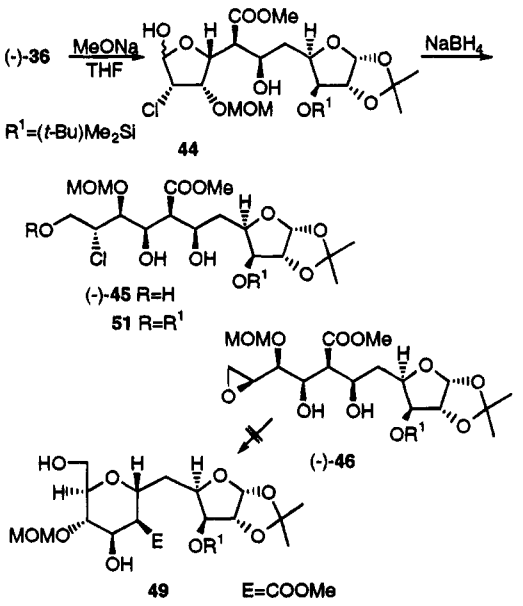
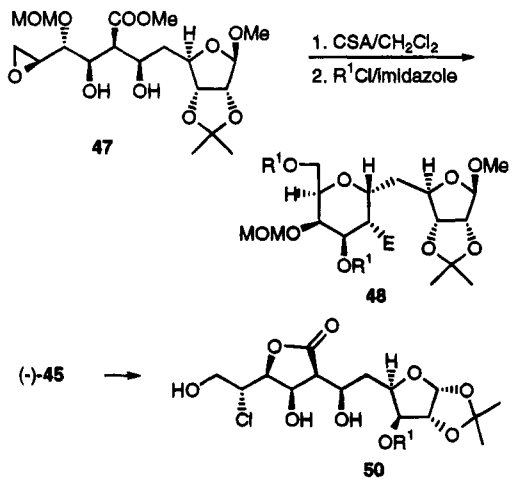
transition state (Zimmerman–Traxler model). By analogy the (3′*R*,6*S*) configuration was assigned to the diastereomeric aldol (−)-**42** but it was not established unequivocally. Baeyer–Villiger oxidation (mCPBA, $NaHCO_3$, CH_2Cl_2, 10 °C) of (−)-**40** furnished uronolactone (−)-**36** (61%), whereas (−)-**42** was converted into (+)-**38** (71%), indicating that the condensations of the lithium enolates of (−)-**33** and (+)-**33** were also highly *exo* face selective and would have transition states similar (Zimmerman–Traxler model, like mode, see Figure 1) to those implied in the lithium enolate of ketone (−)-**30** and (+)-**30**.



Treatment of (−)-**36** with MeONa (THF, −20 °C) gave furanose **44** which was reduced directly by $NaBH_4$ into (−)-**45** (61%, two steps). Elimination of HCl to generate the terminal epoxide (−)-**46** did not succeed with K_2CO_3/MeOH; these conditions led, instead, to γ-lactone **50**. No reaction was observed with Ag_2CO_3/MeOH or DBU/$AgNO_3$/MeOH. A low yield of (−)-**46** was obtained with KH/THF. Finally (−)-**46** was isolated in 84% yield by



treatment of (−)-**45** with BuLi in THF/DMPU (−65° to 0 °C). During our model study[11] we found that the epoxy



diol **47** could be rearranged under acidic conditions (camphorsulfonic acid/CH_2Cl_2, 0 °C) into the corresponding tetrahydropyranyl derivative which was isolated as the disilyl ether **48** (43%) after silylation. Unfortunately, under similar conditions, (−)-**46** failed to give the expected analogue **49** and only products of decomposition were observed. With protic acids such as NH_2SO_3H, Nafion NR50, $HClO_4$, and CF_3COOH or Lewis acids such as $BF_3{\cdot}Et_2O$, $LiClO_4$, $Zn(OTf)_2$, $Ti(O\text{-}i\text{-}Pr)_4$, Al_2O_3, $Al(O\text{-}i\text{-}Pr)_3$, and Me_3SiOTf, (−)-**46** was either unreactive or completely decomposed. We have also selectively protected triol (−)-**46** with (*t*-Bu)Me_2SiCl/imidazole to give **51** and explored the possibility of carrying out intramolecular displacement of the secondary chloride by treatment with BuLi from −65 °C to 25 °C. This also led to decomposition. Since part of the undesired behavior of (−)-**46** might be apportioned to its ester group, which facilitates water elimination, we decided to transform it into a methylidene moiety which is the precursor of the final ulose function. This required the protection of the three alcoholic moieties of (−)-**45** as triethylsilyl ethers, giving (+)-**52** (91%). This compound was then treated with DIBAH (toluene, −65 °C) to furnish the primary alcohol (+)-**53** (77%). Displacement of the alcohol with *o*-nitrobenzeneselenyl cyanide and tributylphosphine,[25] followed by an oxidative workup (mCPBA), provided **54**

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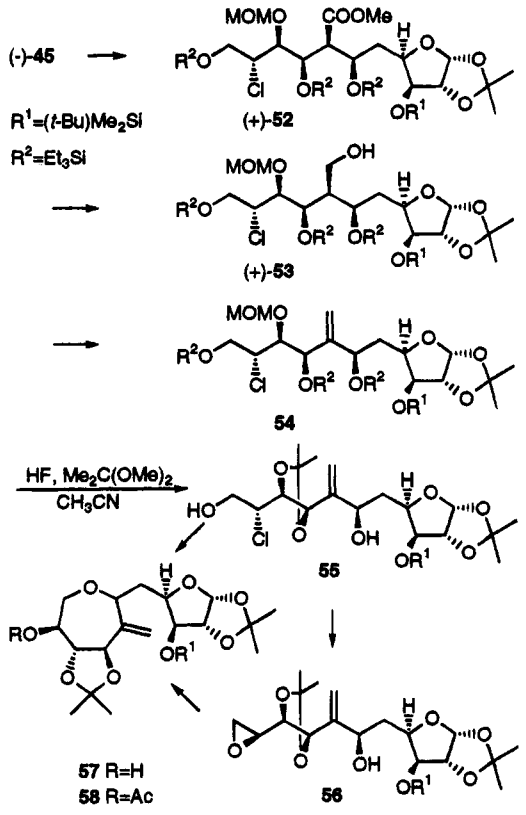

(67%). Selective desilylation and hydrolysis of the MOM ether on treatment with HF/$(MeO)_2CMe_2$/MeCN[26] gave **55** which eliminated HCl (BuLi, THF, DMPU) with formation of epoxide **56** (56%). In the presence of camphorsulfonic acid, **56** was rearranged into oxepane **57** and an unknown epoxide. When **55** was treated with K_2CO_3/MeOH (40 °C), the same oxepane **57** was obtained in 53% yield with no trace of any tetrahydropyranyl derivative. We reasoned that the *trans*-8,9-isopropylidenedioxy moiety impedes the formation of a six-membered ring and allows for the exclusive oxepane formation under basic or acidic conditions. In order to suppress this problem we treated **54** with CsF in DMF thus removing all silyl groups giving the triol epoxide **59**. In the presence of K_2CO_3/MeOH (50 °C) **59** was rearranged into oxepane **60** (80%), characterized as its acetate **61**. Under acidic conditions, **59** failed to give the expected tetrahydropyranyl derivative and only products of decomposition were obtained. We attributed this failure to the trigonal carbon center of **59**. Ozonolysis of **59** furnished hemiacetal (−)-**62** (58%) which could not be isomerized into a tetrahydropyranyl system under acidic conditions. Instead, the spiroacetal **63** was obtained after acetylation (45%, two steps, the configuration of the quaternary center C(7) not being established).

Since neither alkene **59** nor the ketone derived from it by ozonolysis would generate a tetrahydropyranyl system, we decided to maintain a tetrahedral center at C(7) in the form of the arylselenomethyl derivative (+)-**64**. Compound **64** was thus obtained under Grieco's conditions[25] from (+)-**53** in 76% yield. Treatment of (+)-**64**, with CsF in DMF provided the epoxy triol (−)-**65** (78%). Subsequent acid promoted rearrangement with camphorsulfonic acid (2−5 equiv) in CH_2Cl_2 (0−20 °C) provided a 1:2:1 mixture of (−)-**65**, **66**, and **67**. Better conversion rates and selectivities could not be realized.

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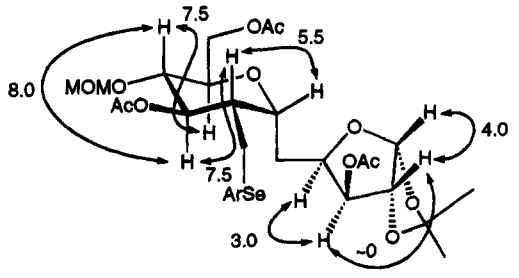
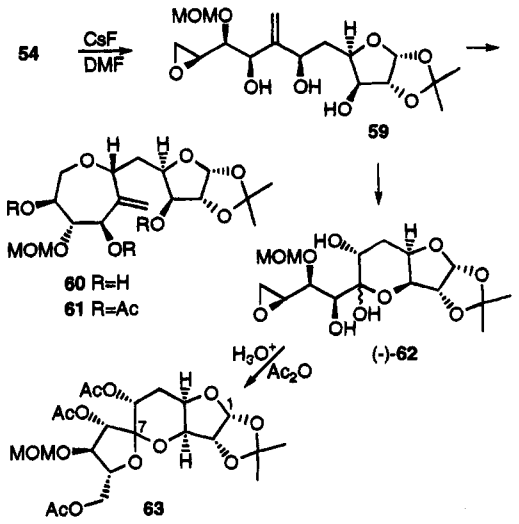


Figure 2. ^3J(H,H) of **69** in hertz.



Attempts with sulfamic acid and Nafion NR50 in CH_2Cl_2 failed to generate the desired compound **66**. Flash chromatography allowed one to separate **67** from the mixture of (−)-**65** and **66**. Acetylation led to a mixture of **68** and **69** that could be separated by chromatography. The structure of **69** was confirmed by its ^{1}H-NMR spectrum which showed signals at δ_H = 5.24 and 5.14 ppm typical of the H-C(8)-OAc and H-C(3)-OAc moieties, respectively. Two less deshielded signals were also observed at δ_H = 4.35 and 3.76 ppm and identified as the new tetrahydropyranyl protons, H-C(6) and H-C(10), respectively.[27] Furthermore the signals of $H_2C(11)$ in **69** were deshielded by ca. 0.5 ppm compared with the H-C(10) signal. Coupling constants between vicinal proton pairs suggested a chair conformation of the α-*C*-pyranosyl moiety as shown in Figure 2. The data also confirmed the (*R*)-configuration of C(6) (see (−)-**40**, *anti*-aldol). Oxidative elimination of the selenium (mCPBA)[25,28] gave alkene (+)-**70** (91%). The ^{1}H-NMR data of (+)-**70**, as well as its NOESY ^{1}H-NMR spectrum were consistent with a $^4C_1$ chair conformation for the α-*C*-pyranosyl moiety. Furthermore, bond C(4)−C(5) adopts an average antiperiplanar position with respect to the C(6)−C(7) bond of the α-*C*-pyranoside as observed for several other α-C-linked disaccharides[27] (see Figure 3). Alkene (+)-**70** was converted into the undeculose derivative (+)-**71** (80%) upon ozonolysis.[29] Similarly, the

(27) For NMR data of C-disaccharides, see e.g.: (a) Wu, T. C.; Goekjian, P. G.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4823. (b) Goekjian, P. G.; Wu, T. C.; Kang, H. Y.; Kishi, Y. *Ibid.* **1991**, *56*, 6422. (c) Wang, Y.; Goekjian, P. G.; Ryckman, D. M.; Miller, W. H.; Bacbirad, S. A.; Kishi, Y. *Ibid.* **1992**, *57*, 482. (d) Oyer, U. C.; Kishi, Y. *Ibid.* **1988**, *53*, 3383. (e) O'Leary, D. J.; Kishi, Y. *Ibid.* **1993**, *58*, 304. (f) Wei, A.; Kishi, Y. *Ibid.* **1994**, *59*, 88. (g) Ferritto, R.; Vogel, P. *Tetrahedron: Asymmetry* **1994**, *5*, 2077.

(28) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947. Grieco, P. A.; Noguez, J. A.; Masaki, Y. *Tetrahedron Lett.* **1975**, *41*, 1485.

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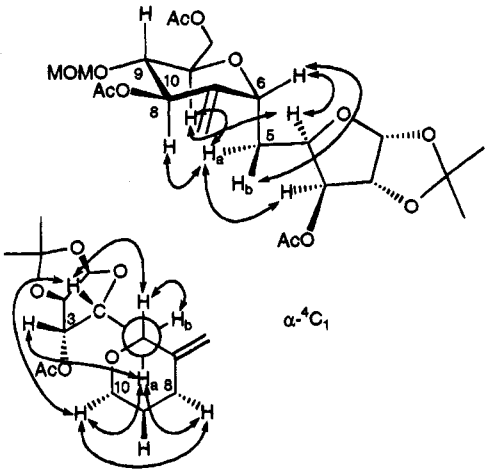


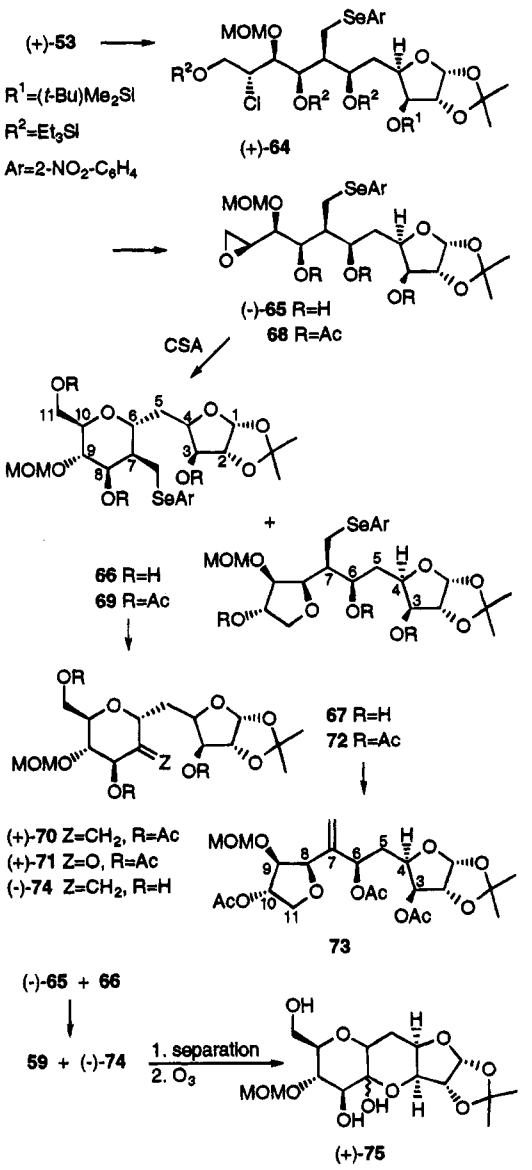
Figure 3. Average conformation of the α-*C*-pyranoside (+)-**70** as suggested by the NOESY ^{1}H-NMR spectrum (double headed arrows indicate the pertinent NOE's) and coupling constants between vicinal protons ($^3J(H_a$-C(5),H-C(6)) = 11.0 Hz, $^3J(H_a$-C(5),H-C(4)) = 4.0 Hz, $^3J(H_b$-C(5), H-C(4)) = 9.0 Hz, $^3J(H_b$-C(5),H-C(6)) = 3.5 Hz).

secondary product **67** was acetylated to provide **72** (82%) and converted into alkene **73** (56%) the structure of which was given by its ^{1}H-NMR spectrum. The relatively highly deshielded protons H-C(3), H-C(6), and H-C(10) at δ_H = 5.54, 5.89, and 5.41 ppm (C_6H_6, 250 MHz), respectively, indicated these positions to be acetylated whereas H-C(8) which resonated at δ_H = 4.91 ppm was indicative of a tetrahydrofuranyl moiety. Furthermore the coupling constants ^3J(H-C(8),H-C(9)) = 3.5 Hz and ^3J(H-C(9),H-C(10)) = 0.5 Hz were consistent with a five-membered ring. Although it was expected that, under acidic conditions, the epoxide ring opening would involve the secondary center C(10) for the intramolecular alcoholysis to the desired tetrahydropyranyl derivative **66,** we observed that this preference was not complete since the primary center C(11) also underwent alcoholysis giving the entropically favored five-membered ring system **67**. This type of rearrangement was not observed in our model study converting **47** → **48**.[11]

When the 1:2 mixture of (−)-**65** and **66** obtained above was treated with mCPBA and then with Et_2NH (to complete the elimination of 2-$NO_2C_6H_4SeOH$), a separable mixture of alkenes **59** and (−)-**74** was obtained. Ozonolysis of (−)-**74** provided the semiprotected undeculose (+)-**75** as a 1.5−2.5:1 anomeric mixture.

Conclusion

A semiprotected form of the undeculose (6,10-anhydro-5-deoxy-7-undeculofuranose-(1,4)-pyranose-(7,3)) of the herbicidins has been prepared in 17 steps and 0.33% overall yield (71% average yield per step) from the racemic Diels−Alder adduct of furan to 1-cyanovinyl acetate and D-glucurono-6,3-lactone. This study has led to the synthesis of 7-oxabicyclo[2.2.1]heptan-2-ones bearing two orthogonal substituents at the *endo* positions of C(5) and C(6). Cross-aldolization of 3-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexodialdo-1,4-furanose ((−)-**6**) with the lithium enolate of (±)-6-*endo*-chloro-5-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**30**) is highly *exo* selective



giving two major diastereomeric aldols (Zimmerman−Traxler model is obeyed) that can be separated. Using a homochiral "naked sugar" such as (1*R*,4*R*)-7-oxabicyclo-[2.2.1]hept-5-en-2-one ((+)-**8**) should avoid the need for a racemate resolution, and the overall yield of the synthesis may potentially be doubled. The *trans*-6,10-tetrahydropyran system is generated through acid-induced epoxide opening of 10,11-anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-[[(2-nitrophenyl)seleno]methyl]-β-L-*ido*-L-*ido*-undecofuranose ((−)-**65**). When position C(7) of this system bears a methylidene group, the rearrangement leads only to the formation of oxepane systems. Unusual carbohydrate analogues have been successfully prepared in this work and our methods should be applicable to the preparation of other diastereomeric derivatives and analogues of the herbicidins.

Experimental Section

General remarks, see ref 30. None of the procedures were optimized. Flash column chromatography (FC) was performed on Merck silica gel (230−400 mesh). Thin layer chromatography (TLC) was carried out on silica gel (Merck aluminum foil). ^{1}H-NMR signal assignments were confirmed by double irradiation experiments and, when required, by 2-D-NOESY spectra.

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3-*O*-(*tert*-Butyldimethylsilyl)-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexodialdo-1,4-furanose ((−)-6). A 1 M solution of diisobutylaluminum hydride (DIBAH, Aldrich, No. 25687-0, 1.94 mL) was added dropwise to a stirred solution of (−)-**18** (610 mg, 1.76 mmol) in anhydrous CH_2Cl_2 (10 mL) cooled to −65 °C (TLC, EtOAc/light petroleum 1:10, R_f ((−)-**18**) = 0.38, R_f ((−)-**6**) = 0.20, vanillin). After stirring at −65 °C for 30 min, MeOH (1 mL) was added and the solution was allowed to warm to 0 °C. A 25% aqueous solution of Rochelle's salt (20 mL) was added and the mixture was stirred vigorously for 90 min. The aqueous layer was extracted with CH_2Cl_2 (10 mL, three times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated to give 542 mg (97.3%), colorless oil pure enough for the aldol condensation. FC (50 g SiO_2, EtOAc/light petroleum 1:10) gave 492 mg (88%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.82 (dd, ^3J = 1.7, 1.3), 5.90 (d, ^3J = 3.5), 4.59 (ddd, ^3J = 6.5, 6.0, 2.5), 4.39 (d, ^3J = 3.5), 4.22 (d, ^3J = 2.5), 2.83 (ddd, ^2J = 18.0, ^3J = 6.0, 1.7), 2.73 (ddd, ^2J = 18.0, ^3J = 6.5, 1.3), 1.51, 1.33 (2 × 3 H, 2 s), 0.89 (9 H, s), 0.13, 0.05 (2 × 3 H, 2 s); $[\alpha]^{25}_D$ = −21.3 (*c* = 1.14, $CHCl_3$).

(+)-1,2-*O*-Isopropylidene-5-*O*-(phenoxythiocarbonyl)-α-D-glucurono-6,3-lactone ((+)-12). A solution of phenoxythiocarbonyl chloride (6.9 mL, 51 mmol) in anhydrous CH_2Cl_2 (25 mL) was added dropwise over *ca.* 20 min. to a stirred solution of 1,2-*O*-isopropylidene-α-D-glucurono-6,3-lactone ((+)-**11**)[15] (10.0 g, 46.3 mmol), anhydrous pyridine (25 mL), and CH_2Cl_2 (25 mL) cooled to 0 °C. After stirring at 0 °C for 30 min, a white precipitate formed. The mixture was then stirred at 20 °C for 2 h (followed by TLC, EtOAc/light petroleum 1:3, R_f ((+)-**11**) = 0.05, R_f ((+)-**12**) = 0.34, vanillin, UV). EtOAc (400 mL) was added and the solution washed with 5% aqueous Na_2CO_3 solution (50 mL) and brine (150 mL). The aqueous phase was extracted with EtOAc (300 mL). The separated organic phases were washed with the same 1 M aqueous HCl solution (125 mL) and brine (250 mL). The combined organic solutions were dried ($MgSO_4$), the solvent was evaporated under reduced pressure and the residue purified by FC (EtOAc/Et_2O 1:3) and crystallized from 1:2 EtOAc/light petroleum giving 18.5 g of white crystals, mp 67−68 °C. Recrystallization from EtOAc/light petroleum gave 15.0 g (92%) of white needles: mp 68−69 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.48−7.17 (5 H, m), 6.12 (d, $^3J(H_4,H_5)$ = 4.0), 6.10 (d, $^3J(H_1,H_2)$ = 3.5), 5.27 (dd, $^3J(H_4,H_5)$ = 4.0, $^3J(H_3,H_4)$ = 3.0), 4.97 (d, ^3J = 3.0), 4.90 (d, ^3J = 3.5), 1.55, 1.38 (2 × 3 H, 2 s); $[\alpha]^{25}_D$ = +93 (*c* = 1.58, CH_2Cl_2).

Methyl 1,2-*O*-Isopropylidene-5-*O*-(phenoxythiocarbonyl)-α-D-glucuronate (16). $NaBH_3CN$ (3.24 g, 43.5 mmol) was added to a stirred solution of (+)-**12** (10.3 g, 29.2 mmol) in MeOH (200 mL) cooled to 0 °C. After stirring at 0 °C for 2 h (TLC, R_f (**16**) = 0.14, R_f ((+)-**12**) = 0.34, EtOAc/light petroleum 1:3) EtOAc (400 mL) was added and the solution washed with 1:1 brine + H_2O (400 mL). The aqueous layer was extracted with EtOAc (200 mL, four times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to give 8.8 g of a yellowish solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.46−7.10 (5 H, m), 6.00 (d, ^3J = 3.5), 5.75 (d, ^3J = 6.0), 4.60 (dd, ^3J = 6.0, 3.0), 4.58 (d, $^3J(H_1,H_2)$ = 3.5), 4.40 (dd, ^3J = 3.0, $^3J(H_3,OH)$ = 6.0), 1.50, 1.32 (2 × 3 H, 2 s).

Methyl 3-*O*-(*tert*-Butyldimethylsilyl)-1,2-*O*-isopropylidene-5-*O*-(phenoxythiocarbonyl)-α-D-glucuronate ((−)-17). The crude solid obtained above was dissolved in anhydrous CH_2Cl_2 (90 mL) and cooled to 0 °C. 2,6-Lutidine (8 mL) was added followed by the dropwise addition of (*t*-Bu)$Me_2SiOSO_2CF_3$ (12.5 mL, 87.6 mmol). After stirring at 0 °C for 2 h (TLC, R_f (**16**) = 0.12, R_f ((−)-**17**) = 0.54, EtOAc/light petroleum 1:4) the mixture was poured into CH_2Cl_2 (400 mL) and ice-cold saturated aqueous $NaHCO_3$ solution (400 mL). The aqueous phase was extracted with CH_2Cl_2 (200 mL, three times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. FC (EtOAc/light petroleum 1:6) gave 8.1 g of a white solid. Recrystallization from light petroleum (30 mL) gave 6.4 g (44%) of colorless prisms: mp 116−117 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.46−7.08 (5 H, m), 6.01 (d, ^3J = 3.5), 5.34 (d, ^3J = 9.5), 4.54 (dd, ^3J = 9.5, 2.5), 4.42 (d, ^3J = 3.5), 4.40 (d, ^3J = 2.5), 3.85 (3 H, s), 1.50, 1.34 (2 × 3 H, 2 s), 0.82 (9 H, s), 0.20, 0.17 (2 × 3 H, 2 s); $[\alpha]^{25}_D$ = −22.1 (*c* = 1.24, $CHCl_3$).

Methyl 3-*O*-(*tert*-Butyldimethylsilyl)-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranuronate ((−)-18). A mixture of (−)-**17** (10.5 g, 21.0 mmol), anhydrous toluene (100 mL), Bu_3SnH (6.15 mL, 23.1 mmol), and azobis(isobutyronitrile) (AIBN, 173 mg, 1.0 mmol) was heated to 80 °C for 2 h (TLC, R_f ((−)-**17**) = 0.26, R_f ((−)-**18**) = 0.29, EtOAc/light petroleum 1:10). The solvent was evaporated under reduced pressure and the residue purified by FC (EtOAc/light petroleum 1:10) giving 5.7 g (78%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (d, ^3J = 3.5), 4.55 (ddd, ^3J = 7.5, 6.5, 3.0), 4.37 (d, ^3J = 3.5), 4.24 (d, ^3J = 3.0), 3.69 (3 H, s), 2.72 (d, *J* = 6.5), 2.70 (d, ^3J = 7.5), 1.51, 1.32 (2 × 3 H, 2 s), 0.89 (9 H, s), 0.12, 0.05 (2 × 3 H, 2 s); $[\alpha]^{25}_D$ = −32.9 (*c* = 0.94, $CHCl_3$).

(±)-(Methyl 5-Deoxy-3-*O*-(methoxymethyl)-β-DL-*xylo*-hexofuranosid)urono-6,3-lactone (19β). A mixture of **22** (32 mg, 0.18 mmol), anhydrous $CHCl_3$ (2 mL), dimethoxymethane (2 mL), and P_2O_5 (0.5 g) was stirred at 20 °C for 10 min. CH_2Cl_2 (10 mL) and ice-cold 5% aqueous Na_2CO_3 solution (10 mL) were added, the latter dropwise under vigourous stirring (CO_2 evolution). The aqueous layer was extracted with CH_2Cl_2 (10 mL, three times). The organic extracts were washed with brine (8 mL). The combined organic solutions were dried ($MgSO_4$), the solvent was evaporated under reduced pressure and the residue purified by FC (10 g of SiO_2, EtOAc/light petroleum 2:1). A first fraction gave 13 mg (32.5%) of pure **19β** as a colorless oil. A second fraction yielded 17 mg (42.5%) of a 1:3 mixture of α- and β-anomers **19α**/**19β**: ^{1}H NMR (250 MHz, $CDCl_3$) of **19β** δ 5.09 (ddd, ^3J = 7.5, 5.5, 1.0), 5.01 (s), 4.93 (d, ^3J = 5.5), 4.75, 4.71 (2d, ^2J = 6.5), 4.31 (s), 3.40, 3.36 (2 × 3 H, 2s), 2.81 (dd, ^2J = 19.0, ^3J = 7.5), 2.64 (dd, ^2J = 19.0, ^3J = 1.0).

(1*RS*,5*SR*,6*SR*,7*SR*)-6,7-*exo*-Epoxy-2,8-dioxabicyclo[3.2.1]-octan-3-one (21). *m*-Chloroperbenzoic acid (mCPBA, 55%, Fluka, No. 25800, 1.37 g, 4.37 mmol) was dissolved in CH_2Cl_2 (10 mL). The aqueous layer was separated and the organic solution dried ($MgSO_4$). $NaHCO_3$ (665 mg, 7.92 mmol) and 5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]heptan-2-one[18] (**20**, 0.5 g, 3.96 mmol) were added at 0 °C. After stirring at 20 °C for 18 h, CH_2Cl_2 (50 mL) was added. The solution was washed with a saturated aqueous solution of $NaHSO_3$ (50 mL) and then with 5% aqueous $NaHCO_3$ (50 mL). The combined aqueous layers were extracted with CH_2Cl_2 (50 mL, three times). The combined organic extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by FC (30 g of SiO_2, EtOAc/light petroleum 1:1) to give 473 mg (84%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.74 (s), 4.58 (d, ^3J = 6.0), 3.92, 3.75 (2d, ^3J = 3.0), 3.02 (dd, ^2J = 18.5, ^3J = 6.0), 2.50 (d, ^2J = 18.5).

(±)-(Methyl 5-Deoxy-α- and β-DL-*xylo*-hexofuranosid)-urono-6,3-lactone (22). A mixture of **21** (370 mg, 2.6 mmol), MeOH (3.7 mL), and $MeSO_3H$ (168 μL, 2.6 mmol) was stirred at 20 °C for 90 min (TLC, EtOAc/light petroleum 1:1, R_f (**21**) = 0.31, R_f (**22**) = 0.13, vanillin). AcONa (260 mg) was added, and the solvent was evaporated under reduced pressure. The residue was diluted with Et_2O (5 mL), and the solution was filtered through Celite. After solvent evaporation, FC (EtOAc/light petroleum 2:1) gave 286 mg (63%) of a 1:7.5 mixture of α- and β-methyl furanoside as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) of the β-anomer δ 5.07 (dd, ^3J = 8.0, 5.5), 4.88 (s), 4.83 (d, ^3J = 5.5), 4.31 (d, $^3J(H_6,OH)$ = 3.0), 3.97 (d, ^3J = 3.0), 3.29 (3 H, s), 2.79 (dd, ^2J = 19.0, ^3J = 8.0), 2.56 (d, ^2J = 19.0).

(1*RS*,2*SR*,3*RS*,4*SR*)-3-*endo*-Chloro-5-oxo-2-*endo*-(phenylseleno)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate ((±)-24), (1*RS*,2*SR*,3*RS*,4*SR*)-3-*endo*-Chloro-5-oxo-2-*endo*-(phenylseleno)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl 3′-Chlorobenzoate ((±)-25), and (1*RS*,4*RS*)-6-Chloro-5-(phenylseleno)-7-oxabicyclo[2.2.1]hept-5-en-2-one (26). A solution of (±)-**23**[20] (4.0 g, 13.3 mmol) in anhydrous THF (16 mL) was added dropwise to a stirred solution of mCPBA (85%, 2.69 g, 14.5 mmol) in anhydrous THF (80 mL) cooled to −65 °C. After stirring at −65 °C for 20 min (TLC, EtOAc/light petroleum 1:4, R_f (**23**) = 0.33, R_f (selenoxide) ≅ 0.0, vanillin), Ac_2O (2.88 mL, 62 mmol) and AcONa (1.44 g, 35 mmol) were added. The cooling bath was removed and the mixture was allowed to

warm to 20 °C over 40 min, after which it was heated to 60 °C for 1 h (R_f (**24**) ≅ 0.23). After cooling to 30 °C, the mixture was poured into EtOAc (400 mL) and the solution was washed with 10% aqueous solution of NaOH (80 mL, three times) and brine (100 mL). The combined aqueous layers were extracted with EtOAc (100 mL, twice). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. FC (280 g SiO_2, EtOAc/light petroleum 1:3) gave a first fraction of 620 mg of a yellow oil which crystallized at 20 °C. Recrystallization from EtOAc/light petroleum yielded 280 mg (7%) of **26**. A second fraction gave 600 mg of a yellowish solid which was recrystallized from EtOAc/light petroleum to give 400 mg (10%) of (±)-**25**. A third fraction afforded 3.24 g (68%) of a solid which was recrystallized from EtOAc/light petroleum giving 2.53 g (53%) of (±)-**24**. Concentration of the mother-liquor yielded 432 mg (9%) of (±)-**24**.

Data for (±)-24: white crystals, mp 137.5−139 °C; ^{1}H NMR (250 MHz, C_6D_6) δ 7.30−7.27 (2 H, m), 7.06−6.90 (3 H, m), 4.39 (dd, ^3J = 6.0, ^4J = 1.8), 4.33 (ddd, ^3J = 6.5, ^4J = 1.8, 1.5), 3.99 (ddd, ^3J = 6.0, ^4J = 1.5, 1.4), 2.99 (d, ^2J = 18.0), 1.95 (ddd, ^2J = 18.0, ^3J = 6.5, ^4J = 1.4), 1.61 (3 H, s).

Data for (±)-25: colorless needles, mp 134−136.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.87−7.83 (2 H, m), 7.62−7.57 (1 H, m), 7.51−7.37 (4 H, m), 7.30−7.23 (2 H, m), 4.83 (ddd, ^3J = 6.0, ^4J = 1.8, ^5J = 0.5), 4.78 (ddd, ^3J = 6.5, ^4J = 1.8, 1.4), 4.51 (ddd, ^3J= 6.0, ^4J = 1.5, 1.4), 3.33 (d, ^2J = 14.0), 2.67 (ddd, ^2J = 14.0, ^3J = 6.5, ^4J = 1.5, ^5J = 0.5).

Data for 26: white crystals, mp 61−62 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.60−7.56 (2 H, m), 7.44−7.33 (3 H, m), 4.91 (dd, ^3J = 4.0, ^4J = 1.0), 4.57 (br s), 2.22 (dd, ^2J = 16.0, ^3J = 4.0), 1.99 (d, ^2J = 16.0).

(1*R*,2*S*,3*R*,4*S*)-3-*endo*-Chloro-5-oxo-2-*endo*-(phenylseleno)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate ((−)-24). This compound was obtained from (−)-**23** following the procedure described for (±)-**24**: colorless needles, mp 127.5−129 °C; $[\alpha]^{25}_D$ = −231, $[\alpha]^{25}_{577}$ = −242, $[\alpha]^{25}_{546}$ = −280, $[\alpha]^{25}_{435}$ = −526, $[\alpha]^{25}_{405}$ −663 (*c* = 1.26, CH_2Cl_2).

(1*R*,2*S*,3*R*,4*S*)-3-*endo*-Chloro-5-oxo-2-*endo*-(phenylseleno)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl 3′-Chlorobenzoate ((−)-25). This compound was prepared as (±)-**25** starting with (−)-**23**. White prisms, mp 131−132.5 °C; $[\alpha]^{25}_D$ = −194, $[\alpha]^{25}_{577}$ = −205, $[\alpha]^{25}_{546}$ = −237, $[\alpha]^{25}_{435}$ = −442, $[\alpha]^{25}_{405}$ −553 (*c* = 1.0, $CHCl_3$).

(1*RS*,2*SR*,3*SR*,4*RS*)-3-*endo*-Chloro-5-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Acetate ((±)-28). A mixture of (±)-**24** (10.0 g, 27.8 mmol), anhydrous toluene (140 mL), Bu_3SnH (8.64 mL, 30.6 mmol), and AIBN (95 mg, 0.56 mmol) was heated to 80 °C for 1 h (TLC, EtOAc/light petroleum 1:3, R_f (**28**) = 0.23, R_f (**24**) = 0.25). The solvent was evaporated under reduced pressure and the residue dissolved in MeCN (300 mL). The solution was extracted with hexane (100 mL, twice). The combined hexane solutions were extracted with MeCN (100 mL). The combined MeCN solutions were evaporated under reduced pressure. FC (400 g SiO_2, EtOAc/light petroleum 1:3) gave 4.9 g (86%) of a colorless oil composed of a 6:1 mixture of (±)-**28** and its *exo* acetate (±)-**29**: ^{13}C NMR (100.61 MHz, $CDCl_3$) of (±)-**28** δ 204.6, 169.7 (2s), 82.2, 76.7, 68.1, 52.0 (4d), 37.3 (t), 20.5 (q).

(1*R*,2*S*,3*S*,4*S*)-3-*endo*-Chloro-5-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Acetate ((+)-28). The same procedure as above starting with (−)-**24** gave a 6:1 mixture of (+)-**28** and **29**. Crystallization from Et_2O and light petroleum at 20 °C gave a 3:1 mixture of (+)-**28** and **29**, mp 53−56 °C. $[\alpha]^{25}_D$= +73 (*c* = 1.1, CH_2Cl_2).

(1*RS*,4*SR*,5*RS*,6*RS*)-6-*endo*-Chloro-5-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]heptan-2-one ((±)-30). (A) A 5.4 M solution of MeONa in MeOH (Fluka, No 71748, 1.2 mL) was added dropwise to a stirred solution of a 6:1 mixture of (±)-**28** and **29** (1.20 g, 5.89 mmol) in anhydrous THF (24 mL) cooled to −25 °C. After stirring at −25 °C for 10 min, the mixture was poured into a saturated aqueous NH_4Cl solution (80 mL) and ice (100 g). The mixture was vigorously stirred and then extracted with CH_2Cl_2 (80 mL, four times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated giving 881 mg (92%) of crude alcohols that were dissolved at 20 °C in CH_2Cl_2 (22 mL) and $(MeO)_2CH_2$ (22 mL). P_2O_5 (6.0 g) was added portionwise under vigorous stirring (10 min). The mixture was poured into CH_2Cl_2 (50 mL), 5% aqueous solution of $NaHCO_3$ (50 mL), and ice (50 g). The flask was carefully rinsed with CH_2Cl_2 (50 mL) and 5% aqueous solution of $NaHCO_3$. The combined aqueous layers were extracted with CH_2Cl_2 (80 mL, three times). The organic phases were washed separately with the same brine (80 mL). The combined organic solutions were dried ($MgSO_4$), and the solvent was evaporated. FC (60 g SiO_2, EtOAc/light petroleum 1:3) gave 931 mg (76.5%) of a yellowish solid composed of a 6:1 mixture of (±)-**30** and **31** (5-epimer of (±)-**30**). Recrystallization from EtOAc/light petroleum gave 737 mg (60%) of colorless crystals: mp 67−68 °C. Concentration of the mother-liquor provided 119 mg of a yellowish oil composed of a 1:1.6 mixture of (±)-**30** and **31**. (B) The same procedure as above starting with (±)-**35** (635 mg, 2.11 mmol) gave 332 mg (76%) of (±)-**30**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.90−4.85 (1 H, m), 4.78, 4.70 (2d, ^2J = 7.0), 4.38−4.37 (3 H, m), 3.40 (3 H, s), 2.71 (d, ^2J = 18.0), 2.44 (dd, ^2J = 18.0, ^3J = 6.5).

(1*R*,4*S*,5*R*,6*R*)-6-*endo*-Chloro-5-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]heptan-2-one ((−)-30). The same procedure (A) as for the preparation of (±)-**30** was used starting with a 6:1 mixture of (+)-**28** and **29**. FC gave a 6:1 mixture of (−)-**30** and **31** (86%) as a colorless oil. Same procedure (B) as for the preparation of (±)-**30**, starting with pure (+)-**35** (92 mg, 0.31 mmol) gave 34 mg (54%) of a colorless oil: $[\alpha]^{25}_D$ = −103, $[\alpha]^{25}_{577}$ = −106, $[\alpha]^{25}_{546}$ = −121, $[\alpha]^{25}_{435}$ = −211, $[\alpha]^{25}_{405}$ −261 (*c* = 0.58, $CHCl_3$).

(1*RS*,5*RS*,6*SR*,7*SR*)-7-*endo*-Chloro-6-*endo*-(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]heptan-3-one ((±)-33). A mixture of (±)-**30** (0.2 g, 0.97 mmol), anhydrous CH_2Cl_2 (2 mL), mCPBA (81%, 227 mg, 1.06 mmol), and $NaHCO_3$ (163 mg, 1.95 mmol) was stirred at 20 °C for 18 h (TLC, EtOAc/light petroleum 1:1, R_f (**30**) = 0.53, R_f (**33**) = 0.28). CH_2Cl_2 (15 mL) was added, and the solution was washed with H_2O (15 mL) and saturated aqueous solution of $NaHCO_3$ (15 mL). The combined aqueous phases were extracted with CH_2Cl_2 (15 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. The residue was recrystallized from EtOAc/light petroleum to give 135 mg (63%) of white crystals: mp 78.5−80 °C. Concentration of the mother liquor furnished a yellowish solid (44 mg). FC (EtOAc/light petroleum 1:1) provided 20 mg (10%) of (±)-**33**. ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.76 (d, ^3J = 4.0), 4.79 (ddd, ^3J = 6.5, 5.5, 1.5), 4.77, 4.68 (2d, ^2J = 7.0), 4.50 (dd, ^3J = 8.5, 6.5), 4.37 (dd, ^3J = 8.5, 4.0), 3.37 (3 H, s), 2.91 (dd, ^2J = 18.0, ^3J = 1.5), 2.89 (dd, ^2J = 18.0, ^3J = 5.5).

(1*S*,5*R*,6*S*,7*S*)-7-*endo*-Chloro-6-*endo*-(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]heptan-3-one ((−)-33) and (1*S*,5*R*,-6*R*,7*S*)-7-*endo*-chloro-6-*exo*-(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]heptan-3-one (34). Same procedure as for the preparation of (±)-**33**, starting with a 6:1 mixture of (−)-**30** and **31** (250 mg, 1.2 mmol). FC (20 g SiO_2, EtOAc/light petroleum 1:1); first fraction: 37 mg (16%) of **34**, second fraction: 205 mg (88%) of (−)-**33**, the latter was recrystallized from toluene at −20 °C, to give 118 mg (50%) of white needles. Concentration of the mother liquor provided 68 mg of (−)-**33**. $[\alpha]^{25}_D$= −194 (*c* = 1.17, $CHCl_3$).

Data for 34: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (dd, ^3J = 4.0, ^4J = 1.0), 4.78, 4.72 (2d, ^2J = 7.0), 4.64 (ddd, ^3J = 7.0, ^4J 1.0, 0.8), 4.29 (ddd, ^3J = 4.0, 3.0, ^4J = 0.8), 4.15 (d, ^3J = 3.0), 3.42 (3 H, s), 3.13 (dd, ^2J = 18.0, ^3J = 7.0), 2.67 (d, ^2J = 18.0).

(1*RS*,2*SR*,3*SR*,4*RS*)-3-*endo*-Chloro-5-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl 3′-Chlorobenzoate ((±)-35). The same procedure as that used for (±)-**28**, starting with (±)-**25** gave a white solid, 829 mg (73%). Recrystallization from EtOAc/light petroleum gave 708 mg (63%) of white crystals: mp 132−134 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.98 (dd, ^4J = 2.0, 1.5), 7.92 (ddd, ^3J = 8.0, ^4J = 2.0, 1.5), 7.58 (ddd, ^3J = 8.0, ^4J = 2.0, 1.0), 7.42 (t, ^3J = 8.0), 5.49 (ddd, ^3J = 8.0, 5.0, ^4J = 0.7), 5.13 (dddd, ^3J = 5.5, 5.0, ^4J = 1.0, 0.6), 4.60 (dddd, ^3J = 8.0, 6.0, ^4J = 0.6, ^5J = 0.5), 4.52 (br d, ^3J = 6.0), 2.72 (br d, ^2J = 18.0), 2.60 (dddd, ^2J = 18.0, ^3J = 5.5, ^4J = 0.7, ^5J = 0.5).

(1*R*,2*S*,3*S*,4*R*)-3-*endo*-Chloro-5-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl 3′-Chlorobenzoate ((+)-35). The same procedure as that used for (±)-**35** but starting with (−)-**25**. White

crystals: mp 99–103 °C. $[\alpha]^{25}_D = +22.8$, $[\alpha]^{25}_{577} = +23.0$, $[\alpha]^{25}_{546} = +26.2$, $[\alpha]^{25}_{435} = +40$, $[\alpha]^{25}_{405} = +43$ ($c = 0.95$, $CHCl_3$).

(6*R*)-3-*O*-(*tert*-Butyldimethylsilyl)-6-*C*-[(1′*S*,4′*S*,5′*R*,6′*S*,7′*S*)-7′-*endo*-chloro-6′-*endo*-(methoxymethoxy)-3′-oxo-2′,8′-dioxabicyclo[3.2.1]oct-4′-*exo*-yl]-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose ((−)-36). A mixture of (−)-**40** (756 mg, 1.45 mmol), anhydrous CH_2Cl_2 (2.5 mL), mCPBA (85%, 1.46 g, 7.3 mmol), and $NaHCO_3$ (1.21 g, 14.5 mmol) was stirred at 20 °C for 18 h (TLC, EtOAc/light petroleum 1:1, R_f(**40**) = 0.25, R_f(**36**) = 0.37, vanillin). CH_2Cl_2 (70 mL) was added. The solution was washed with a half-saturated aqueous solution of $NaHSO_3$ (70 mL) and then with a saturated aqueous solution of $NaHCO_3$ (70 mL). The aqueous layers were extracted with CH_2Cl_2 (70 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (70 g SiO_2, EtOAc/light petroleum 1:1) gave 700 mg (89%) of a white solid which was recrystallized from Et_2O/light petroleum to give 600 mg (76%) of white prisms: mp 91–94 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88 (d, ^3J = 4.0), 5.76 (d, ^3J = 4.0), 4.89 (d, ^3J = 6.5), 4.79, 4.69 (2d, ^2J = 7.0), 4.53 (dd, ^3J = 8.5, 6.5), 4.50–4.38 (2 H, m), 4.38 (dd, ^3J = 8.5, 4.0), 4.36 (d, ^3J = 4.0), 4.07 (d, ^3J = 3.5), 3.38 (3 H, s), 3.12 (d, ^3J = 4.5), 1.93–1.87 (2 H, m), 1.49, 1.31 (2 × 3 H, 2s), 0.90 (9 H, s), 0.12, 0.11 (2 × 3 H, 2s). $[\alpha]^{25}_D = -75.7$ ($c = 1.17$, $CHCl_3$).

(6*S* or 6*R*)-3-*O*-(*tert*-Butyldimethylsilyl)-6-C-[(1′*R*,4′*R*,5′*S*,6′*R*,7′*R*)-7′-*endo*-chloro-6′-*endo*-(methoxymethoxy)-3′-oxo-2′,8′-dioxabicyclo[3.2.1]oct-4′-*exo*-yl]-5-deoxy-1,2-*O*-isopropylidene-αf-D-*xylo*-hexofuranose ((+)-38). (A) BuLi (1.6 M in hexane, Fluka No 20160, 0.17 mL, 0.27 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2NH$ (66 μL, 0.32 mmol) in anhydrous THF (1.5 mL) cooled to −10 °C under an Ar atmosphere. After stirring at −10 °C for 15 min the solution was cooled to −65 °C and (±)-**33** (50 mg, 0.23 mmol), in anhydrous THF (1 mL), was added dropwise. After stirring at −65 °C for 30 min, (−)-**6** (35.5 mg, 0.12 mmol), dissolved in anhydrous THF (0.5 mL), was added dropwise. After stirring at −65 °C for 1 h, the mixture was poured into CH_2Cl_2 (10 mL), a saturated aqueous solution of NH_4Cl (10 mL) and ice (20 g). The aqueous layer was extracted with CH_2Cl_2 (10 mL, three times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (10 g SiO_2, EtOAc/light petroleum 1:1) gave a first fraction of 37 mg (30% based on converted (±)-**33**) of (+)-**38**. The second fraction furnished 30 mg (25% based on converted (±)-**33**) of (−)-**36**. A third fraction provided 29 mg of (±)-**33** containing 10% of (−)-**36** (conversion rate of (±)-**33**: 46%). (B) Same procedure as for the preparation of (−)-**36**, starting with aldol (−)-**42** (600 mg, 1.15 mmol) (TLC, EtOAc/light petroleum 1:2, R_f(**42**) = 0.25, R_f(**38**) = 0.39, vanillin). FC gave 377 mg (61%, 75% based on converted (−)-**42**) of a colorless solid: mp 115–117 °C. Recrystallization from EtOAc/light petroleum gave 330 mg (53%, 66% based on converted (−)-**42**), white needles: mp 120–121 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88 (d, ^3J = 3.5), 5.74 (d, ^3J = 4.0), 5.00 (d, ^3J = 6.5), 4.77, 4.59 (2d, ^2J = 7.0), 4.51 (dd, ^3J = 9.0, 6.5), 4.48 (ddd, ^3J= 9.8, 5.5, 1.5), 4.41 (dd, ^3J = 9.0, 4.0), 4.32 (d, ^3J = 3.5), 4.30 (ddd, ^3J = 10.0, 2.5, 2.0), 4.05 (d, ^3J = 2.5), 3.58 (s), 3.40 (3 H, s), 3.36 (d, ^3J = 5.5), 2.84 (ddd, ^2J = 15.0, ^3J= 10.0, 9.8), 1.61 (ddd, ^2J = 15.0, ^3J = 2.0, 1.5), 1.47, 1.30 (2 × 3 H, 2s), 0.89 (9 H, s), 0.10, 0.08 (2 × 3 H, 2s). $[\alpha]^{25}_D = +57.5$.

(6*R*)-3-*O*-(*tert*-Butyldimethylsilyl)-6-*C*-[(1′*R*,3′*S*,4′*R*,5′*S*,6′*S*)-6′-*endo*-chloro-5′-*endo*-(methoxymethoxy)-2′-oxo-7′-oxabicyclo[2.2.1]hept-3′-*exo*-yl]-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose ((−)-40) and (6*S* or 6*R*)-3-*O*-(*tert*-Butyldimethylsilyl)-6-*C*-[(1′*S*,3′*R*,4′*S*,5′*R*,6′*R*)-6′-*endo*-chloro-5′-*endo*-(methoxymethoxy)-2′-oxo-7′-oxabicyclo[2.2.1]hept-3′-*exo*-yl]-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose ((−)-42). 1.6 M BuLi in hexane (Fluka No 20160, 5.6 mL, 8.96 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2NH$ (2.2 mL, 10.5 mmol) in anhydrous THF (47 mL) cooled to −10 °C (three-necked flask dried in a flame) under an Ar atmosphere. After stirring at −10 °C for 10 min, a solution of (±)-**30** (1.55 g, 7.50 mmol) in anhydrous THF (31 mL) was added slowly with stirring at −10 °C. After stirring at −10 °C for 1 h, the mixture was cooled to −65 °C and (−)-**6** (2.85 g, 9 mmol), dissolved in anhydrous THF (17 mL), was added slowly. After stirring at −65 °C for 3 h, the mixture was poured into CH_2Cl_2 (200 mL), a saturated aqueous solution of NH_4Cl (200 mL) and ice (100 g). The aqueous layer was extracted with CH_2Cl_2 (170 mL, three times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (500 g SiO_2, EtOAc/light petroleum 1:2, R_f ((±)-**30**) = 0.35, R_f ((−)-**40**) = 0.27, R_f ((−)-**42**) = 0.39, vanillin) gave a first fraction containing 1.57 g of a 1:7.5 mixture of (±)-**30** and aldol (−)-**42**. Crystallization from Et_2O (5 mL) and light petroleum (20 mL) afforded 1.23 g (32.5%) of (−)-**42**. A second fraction contained 1.76 g (45%) of a 16:1 mixture of (−)-**40** and **43**. Crystallization from Et_2O (1 mL) and light petroleum (15 mL) at −18 °C furnished 1.43 g (36%) of (−)-**40**. Concentration of the mother liquors gave 172 mg of a 2:1 mixture of (−)-**40** and **43**.

Data for (−)-40: white crystals, mp 102.5–104 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (d, ^3J = 4.0), 4.77, 4.69 (2d, ^2J = 7.0), 4.74 (dd, ^3J = 4.0, ^4J = 1.5), 4.43 (ddd, ^3J = 9.0, 3.5, 3.0), 4.42–4.35 (3 H, m), 4.36 (d, ^3J = 4.0), 4.25 (br ddd, ^3J = 10.0, 7.0, 2.5), 3.67 (d, ^3J = 3.0), 3.39 (3 H, s), 2.99 (br s, OH), 2.75 (d, ^3J = 7.0), 1.89 (ddd, ^2J = 14.0, ^3J = 9.0, 2.5), 1.76 (ddd, ^2J = 14.0, ^3J = 10.0, 3.5), 1.49, 1.31 (2 × 3 H, 2s), 0.89 (9 H, s), 0.12, 0.09 (2 × 3 H, 2s). $[\alpha]^{25}_D = -8.4$ ($c = 1.18$, $CHCl_3$).

Data for (−)-42: white needles, mp 91.5–93 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.89 (d, ^3J = 3.5), 4.89 (br d, ^3J = 3.0), 4.79, 4.71 (2d, ^2J = 7.0), 4.39–4.37 (3 H, m), 4.33 (d, ^3J = 3.5), 4.34–4.28 (2 H, m), 4.05 (d, ^3J = 2.5), 3.43 (d, ^3J = 4.0), 3.42 (3 H, s), 3.00 (d, ^3J = 5.5), 2.03 (ddd, ^2J = 14.5, ^3J = 10.0, 9.5), 1.59 (ddd, ^2J = 14.5, ^3J = 3.0, 2.5), 1.49, 1.31 (2 × 3 H, 2s), 0.90 (9 H, s), 0.11, 0.08 (2 × 3 H, 2s). $[\alpha]^{25}_D = -13.2$ (c = 1.41, $CHCl_3$).

3-*O*-(*tert*-Butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-1,2-*O*-isopropylidene-7-*C*-(methoxycarbonyl)-9-*O*-(methoxymethyl)-α-D-*gluco*-L-*ido*-undecofuranose ((−)-45). MeONa (5.4 M in MeOH, 254 μL, 1.49 mmol) was added dropwise to a vigorously stirred solution of (−)-**36** (669 mg, 1.24 mmol) in anhydrous THF (9.4 mL) cooled to −20 °C. After stirring at −20 °C for 10 min the temperature was allowed to reach −5 °C and the mixture was poured into ice-cold EtOAc (50 mL), a saturated aqueous solution of NH_4Cl (50 mL), and ice (50 g). The aqueous layer was extracted with EtOAc (30 mL, four times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to give 595 mg (84%) of **44**. After dissolution in anhydrous MeOH (60 mL) at 0 °C, $NaBH_4$ (119 mg, 3.7 mmol) was added and the mixture stirred at 0 °C for 10 min (TLC, EtOAc/light petroleum 2:1, R_f (**44**) = 0.45, R_f (**45**) = 0.32). The mixture was poured into 0.5 N aqueous HCl (40 mL) and ice (20 g) and extracted with EtOAc (40 mL, five times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. FC (30 g SiO_2, EtOAc/light petroleum 1:1) gave 371 mg (66%) of a white solid: mp 47–49 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.86 (d, ^3J = 4.0), 4.80, 4.74 (2d, ^2J = 6.5), 4.42 (ddd, ^3J = 9.5, 8.0, 1.0), 4.39 (ddd, ^3J = 9.5, 3.0, 2.5), 4.34 (d, ^3J = 4.0), 4.25 (dt, ^3J = 7.5, 4.0), 4.15 (dddd, ^3J = 10.5, 8.0, 3.5, 2.5), 4.04 (d, ^3J = 2.5), 3.95 (dd, ^3J = 7.5, 1.0), 3.98, 3.90 (2 H, m), 3.73 (3 H, s), 3.43 (3 H, s), 3.17 (d, ^3J = 8.0), 3.12 (d, ^3J = 9.5), 3.03 (t, ^3J = 7.0), 2.81 (dd, ^3J = 8.0, 3.5), 1.86 (ddd, ^2J = 14.0, ^3J = 9.5, 2.5), 1.54 (ddd, ^2J = 14.0, ^3J = 10.5, 3.0), 1.48, 1.30 (2 × 3 H, 2s), 0.89 (9 H, s), 0.11, 0.07 (2 × 3 H, 2s). $[\alpha]^{25}_D = -12.4$ (c = 1.04, $CHCl_3$).

10,11-Anhydro-3-*O*-(*tert*-butyldimethylsilyl)-5,7-dideoxy-1,2-*O*-isopropylidene-7-*C*-(methoxycarbonyl)-9-*O*-(methoxymethyl)-β-L-*ido*-L-*ido*-undecofuranose ((−)-46). 1.6 M BuLi in hexane (Fluka No 20160, 1.66 mL, 2.65 mmol) was added dropwise to a stirred solution of (−)-**45** (510 mg, 0.87 mmol) in anhydrous THF (7.6 mL) and DMPU (2.55 mL) cooled to −65 °C. After stirring at −65 °C for 10 min, the mixture was stirred at 0 °C for 1 h. AcOH (0.18 mL) and Et_2O (35 mL) were added. The solution was washed with H_2O (35 mL). The aqueous layer was extracted with Et_2O (30 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (40 g SiO_2, EtOAc/light petroleum 2:1) gave 409 mg (84%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.84 (d, ^3J = 4.0), 4.89, 4.73 (2 d, ^2J =

6.5), 4.36 (ddd, ^3J = 9.5, 3.0, 2.5), 4.33 (d, ^3J = 4.0), 4.17–4.10 (2 H, m), 4.01 (d, ^3J = 2.5), 3.71 (3 H, s), 3.43 (d, ^3J = 9.0), 3.38 (4 H, s), 3.20 (ddd, ^3J = 7.0, 4.5, 2.5), 3.15 (d, ^3J = 7.5), 2.79 (dd, ^2J = 4.7, ^3J = 4.5), 2.77 (dd, ^3J = 6.0, 3.5), 2.62 (dd, ^2J = 4.7, ^3J = 2.5), 1.86 (ddd, ^2J = 14.0, ^3J = 9.5, 2.5), 1.53 (ddd, ^2J = 14.0, ^3J = 10.0, 3.0), 1.46, 1.28 (2 × 3 H, 2s), 0.87 (9 H, s), 0.09, 0.06 (2 × 3 H, 2s). $[\alpha]^{25}_D$ = −23.5 (*c* = 0.80, $CHCl_3$).

9,7-(Carboxy)-anhydro-3-*O*-(*tert*-butyldimethylsilyl)-7-*C*-carboxy-10-chloro-5,7,10-trideoxy-1,2-*O*-isopropylidene-α-D-*gluco*-L-*ido*-undecofuranose (50). A mixture of (−)-**45** (33 mg, 0.057 mmol), anhydrous MeOH (0.3 mL), and K_2CO_3 (16 mg) was heated to 40 °C for 2 h (TLC, EtOAc/light petroleum 1:1, R_f (**45**) = 0.15, R_f (**50**) = 0.26). The mixture was poured into 0.5 N aqueous HCl (10 mL) and EtOAc (10 mL). The aqueous layer was extracted with EtOAc (7 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (15 g of SiO_2, EtOAc/light petroleum 1:1) gave 9 mg (31%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.90 (d, ^3J = 4.0), 4.70 (ddd, ^3J = 4.5, 4.0, 3.0), 4.48 (dd, ^3J = 10.0, 3.0), 4.43–4.35 (3 H, m), 4.38 (d, ^3J = 4.0), 4.10 (d, ^3J = 2.5), 4.07 (2 H, m), 3.80 (d, ^3J = 4.0), 3.69 (d, ^3J = 2.5), 2.70 (dd, ^3J = 7.0, 4.5), 2.15 (t, ^3J = 6.5), 2.01 (dd, ^3J = 4.5, 2.5), 1.99 (d, ^3J = 5.0), 1.50, 1.32 (2 × 3 H, 2s), 0.91 (9 H, s), 0.14, 0.11 (2 × 3 H, 2s).

3,11-Di-*O*-(*tert*-butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-1,2-*O*-isopropylidene-7-*C*-(methoxycarbonyl)-9-*O*-(methoxymethyl)-α-D-*gluco*-L-*ido*-undecofuranose (51). A mixture of (−)-**45** (25 mg, 0.044 mmol), DMF (0.2 mL), (*t*-Bu)Me_2SiCl (16.4 mg, 0.11 mmol), and imidazole (14.8 mg, 0.22 mmol) was stirred at 20 °C for 90 min. Et_2O (10 mL) was added, and the solution was washed successively with brine (2.5 mL), 2 N aqueous HCl (4 mL), a 10% aqueous solution of K_2CO_3 (4 mL), and brine (2.5 mL). The aqueous layers were combined and extracted with Et_2O (10 mL, twice). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (15 g of SiO_2, EtOAc/light petroleum 1:2) gave 20 mg (67%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (d, ^3J = 4.0), 4.86, 4.73 (2d, ^2J = 6.5), 4.43–4.38 (2 H, m), 4.36 (d, ^3J = 4.0), 4.19–4.11 (2 H, m), 4.07 (d, ^3J = 2.5), 3.96–3.94 (3 H, m), 3.74 (3 H, s), 3.43 (3 H, s), 3.19 (d, ^3J = 7.5), 3.17 (d, ^3J = 8.0), 2.84 (dd, ^3J = 7.5, 3.0), 1.85 (ddd, ^2J = 14.5, ^3J = 9.0, 2.5), 1.61 (ddd, ^2J = 14.5, ^3J = 10.5, 3.5), 1.50, 1.31 (2 × 3 H, 2s), 0.91, 0.90 (2 × 9 H, 2s), 0.12, 0.11, 0.10, 0.09 (4 × 3 H, 4s).

3-*O*-(*tert*-Butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-6,8,11-tri-*O*-(triethylsilyl)-1,2-*O*-isopropylidene-7-*C*-(methoxycarbonyl)-9-*O*-(methoxymethyl)-α-D-*gluco*-L-*ido*-undecofuranose ((+)-52). A mixture of (−)-**45** (523 mg, 0.91 mmol), anhydrous pyridine (5 mL), and Et_3SiCl (1.84 mL, 10.9 mmol) was stirred at 20 °C for 18 h. CH_2Cl_2 (50 mL) was added, and the solution was washed with half-saturated aqueous solution of NH_4Cl (150 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL, three times). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. FC (30 g of SiO_2, EtOAc/light petroleum 1:15) gave 761 mg (91%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.86 (d, ^3J = 4.0), 4.83, 4.69 (d, ^2J = 6.0), 4.54 (dd, ^3J = 9.0, 2.0), 4.33 (d, ^3J = 4.0), 4.25 (ddd, ^3J = 10.0, 3.0, 2.0), 4.21 (ddd, ^3J = 10.5, 2.5, 2.0), 4.07–3.90 (4 H, m), 3.98 (d, ^3J = 2.5), 3.70 (3 H, s), 3.38 (3 H, s), 2.98 (dd, ^3J = 9.0, 3.0), 1.97 (ddd, ^2J = 14.5, ^3J = 10.5, 2.0), 1.50 (ddd, ^2J = 14.5, ^3J = 10.0, 2.0), 1.49, 1.30 (2 × 3 H, 2s), 1.00–0.92 (27 H, m), 0.91 (9 H, s), 0.74–0.62 (18 H, m), 0.12, 0.09 (2 × 3 H, 2s). $[\alpha]^{25}_D$ = +12.1 (*c* = 1.0, $CHCl_3$).

3-*O*-(*tert*-Butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-6,8,11-tri-*O*-(triethylsilyl)-7-*C*-(hydroxymethyl)-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-α-D-*gluco*-L-*ido*-undecofuranose ((+)-53). A 1 M solution of DIBAH in toluene (Aldrich, No 25687-0, 1.52 mL, 1.52 mmol) was added dropwise to a stirred solution of (+)-**52** (532 mg, 0.58 mmol) in anhydrous toluene (9 mL) cooled to −65 °C. After stirring at −65 °C for 30 min (TLC, EtOAc/light petroleum 1:15, R_f (**52**) = 0.30, R_f (**53**) = 0.18) MeOH (0.5 mL) was added dropwise; the mixture was poured into 0.5 N aqueous HCl (40 mL) and ice (40 g). The mixture was extracted with CH_2Cl_2 (40 mL, four times). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. FC (30 g SiO_2, EtOAc/light petroleum 1:12) gave 400 mg (77%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.85 (d, ^3J = 4.0), 4.83, 4.69 (2d, ^2J = 6.0), 4.39 (dd, ^3J = 8.0, 2.0), 4.33 (d, ^3J = 4.0), 4.25–4.18 (2 H, m), 4.07 (1 H, m), 4.01–3.77 (4 H, m), 4.00 (d, ^3J = 2.5), 3.87 (dd, ^3J = 8.0, 2.0), 3.37 (3 H, s), 3.28 (dd, ^2J = 8.0, ^3J = 2.0), 1.98 (ddd, ^2J = 14.5, ^3J = 10.5, 4.0), 1.94 (1 H, m), 1.68 (ddd, ^2J = 14.5, ^3J = 8.0, 1.5), 1.48, 1.30 (2 × 3 H, 2s), 1.02–0.94 (27 H, m), 0.90 (9 H, s), 0.84–0.59 (18 H, m), 0.13, 0.10 (2 × 3 H, 2s). $[\alpha]^{25}_D$ = +9.1 (*c* = 1.0, $CHCl_3$).

3-*O*-(*tert*-Butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-6,8,11-tri-*O*-(triethylsilyl)-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-methylidene-α-D-*arabino*-L-*ido*-undecofuranose (54). mCPBA (55%, Fluka No 25800, 59 mg, 0.19 mmol) was added portionwise to a stirred solution of (+)-**64** in CH_2Cl_2 (1.65 mL) and a saturated aqueous solution of $NaHCO_3$ (0.55 mL) cooled to 0 °C. After stirring at 20 °C for 30 min, CH_2Cl_2 (8 mL) and a saturated aqueous solution of $NaHCO_3$ (5 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (8 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (10 g SiO_2, EtOAc/light petroleum 1:19) gave 50 mg (67%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (d, ^3J = 4.0), 5.31 (2 H, br d), 4.71, 4.66 (2d, ^2J = 6.5), 4.67 (d, ^3J = 4.0), 4.45 (dd, ^3J = 10.0, 2.0), 4.35 (d, ^3J = 4.0), 4.29 (ddd, ^3J = 9.0, 2.7, 2.5), 4.10 (ddd, ^3J = 6.5, 6.0, 3.5), 4.08 (dd, ^2J = 11.5, ^3J = 3.5), 4.02 (d, ^3J = 2.7), 3.87 (dd, ^3J= 6.0, 4.0), 3.84 (dd, ^2J = 11.5, ^3J = 6.5), 3.38 (3 H, s), 2.00 (ddd, ^2J = 14.0, ^3J = 9.0, 2.0), 1.66 (ddd, ^2J = 14.0, ^3J = 10.0, 2.5), 1.50, 1.31 (2 × 3 H, 2s), 1.00–0.92 (27 H, m), 0.90 (9 H, s), 0.73–0.61 (18 H, m), 0.13, 0.09 (2 × 3 H, 2s).

3-*O*-(*tert*-Butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-1,2:8,9-di-*O*-isopropylidene-7-*C*-methylidene-α-D-*arabino*-L-*ido*-undecofuranose (55). A mixture of **54** (96 mg, 0.18 mmol), MeCN (1.6 mL), $(MeO)_2CMe_2$ (0.24 mL), and a 40% aqueous solution of HF (32 μL) was heated to 40 °C for 1 h. H_2O (10 mL) was added and the mixture extracted with CH_2Cl_2 (10 mL, four times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (60 g SiO_2, EtOAc/light petroleum) gave 44 mg (76%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.89 (d, ^3J = 3.5), 5.46, 5.40 (2 H, 2s), 4.64 (d, ^3J = 7.0), 4.55 (br dd, ^3J = 8.5, 3.0), 4.40 (ddd, ^3J = 10.0, 3.0, 2.5), 4.39 (dd, ^3J = 7.0, 6.5), 4.35 (d,^3J = 3.5), 4.12 (dt, ^3J = 6.5, 6.0), 4.06 (d, ^3J = 2.5), 3.90 (2 H, br t), 2.11 (ddd, ^2J = 14.5, ^3J = 10.0, 3.0), 1.80 (ddd, ^2J = 14.5, ^3J = 8.5, 3.0), 1.48, 1.43, 1.42, 1.32 (4 × 3 H, 4s), 0.90 (9 H, s), 0.12, 0.09 (2 × 3 H, 2s).

10,11-Anhydro-3-*O*-(*tert*-butyldimethylsilyl)-5,7-dideoxy-1,2:8,9-di-*O*-isopropylidene-7-*C*-methylidene-β-L-*xylo*-L-*ido*-undecofuranose (56). 1.6 M BuLi in hexane (Fluka No 20160, 31 μL, 0.05 mmol) was added dropwise to a stirred solution of **55** (11.5 mg, 0.024 mmol) in anhydrous THF (0.15 mL) and DMPU (0.05 mL). After stirring at 50 °C for 2 h the mixture was poured into a saturated aqueous solution of NH_4Cl (6 mL) and extracted with CH_2Cl_2 (6 mL, 4 times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (5 g, SiO_2, EtOAc/light petroleum 1:2) gave 6 mg (56%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.89 (d, ^3J = 4.0), 5.38, 5.21 (2 H, 2 br s), 4.60 (d, ^3J = 8.5), 4.54 (ddd, ^3J = 7.5, 7.0, 3.5), 4.42 (ddd, ^3J = 10.0, 2.8, 2.5), 4.36 (d, ^3J = 4.0), 4.07 (d, ^3J = 2.8), 3.81 (dd, ^3J = 8.5, 4.5), 3.08 (ddd, ^3J = 4.5, 4.0, 2.5), 2.94 (d, ^3J = 7.0), 2.91 (dd, ^2J = 5.0, ^3J = 4.0), 2.75 (dd, ^2J = 5.0, ^3J = 2.5), 2.17 (ddd, ^2J = 14.0, ^3J = 10.0, 3.5), 1.86 (ddd, ^2J = 14.0, ^3J = 7.5, 2.5), 1.49, 1.43, 1.40, 1.33 (4 × 3 H, 4s), 0.92 (9 H, s), 0.12, 0.09 (2 × 3 H, 2s).

6,11-Anhydro-3-*O*-(*tert*-butyldimethylsilyl)-5,7-dideoxy-1,2:8,9-di-*O*-isopropylidene-7-*C*-methylidene-β-L-*xylo*-L-*ido*-undecofuranose (57). A mixture of **55** (15 mg, 0.029 mmol), anhydrous MeOH (0.3 mL), and K_2CO_3 (8 mg) was stirred at 40 °C for 24 h. After cooling to 20 °C it was poured into 0.5 N aqueous HCl (6 mL) and extracted with CH_2Cl_2 (6 mL, four times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (5 g SiO_2, EtOAc/light petroleum 1:2) gave 8 mg (53%) of a colorless oil: ^{1}H NMR (250 MHz, C_6D_6) δ 6.04 (d, ^3J = 4.0), 5.55, 4.89 (2 H,

2 br s), 4.74 (ddd, ^3J = 9.0, 3.5, 2.5), 4.67 (d, ^3J = 9.0), 4.49 (br dd, ^3J = 10.5, 3.0), 4.46 (d, ^3J = 4.0), 4.14 (d, ^3J= 2.5), 3.98 (dd, ^3J = 12.0, 4.0), 3.87 (ddd, ^3J = 9.5, 8.5, 4.0), 3.46 (dd, ^3J = 9.0, 8.5), 3.07 (dd, ^2J = 12.0, ^3J = 9.5), 2.22 (ddd, ^2J = 14.5, ^3J = 9.0, 3.0), 2.03 (ddd, ^2J = 14.5, ^3J = 10.5, 3.5), 1.57, 1.44, 1.41, 1.21 (4 × 3 H, 4s), 0.93 (9 H, s), 0.01, −0.02 (2 × 3 H, 2s).

10-*O*-Acetyl-6,11-anhydro-3-*O*-(*tert*-butyldimethylsilyl)-5,7-dideoxy-1,2:8,9-di-*O*-isopropylidene-7-*C*-methylidene-β-L-*xylo*-L-*ido*-undecofuranose (58). A mixture of **57** (8 mg, 0.015 mmol), anhydrous THF (0.1 mL), pyridine (15 μL), Ac_2O (15 μL), and 4-(dimethylamino)pyridine (1 mg) was stirred at 20 °C for 1 h. The solvent was evaporated under reduced pressure. FC (EtOAc/light petroleum 1:2) gave 6 mg (68%) of a yellowish oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88 (d, ^3J = 3.5), 5.41, 5.00 (2 H, 2s), 5.02 (ddd, ^3J = 10.5, 9.0, 4.5), 4.50 (br d, ^3J = 8.8), 4.39−4.32 (2 H, m), 4.36 (d, ^3J = 3.5), 4.03 (d, ^3J = 2.5), 4.02 (dd, ^2J = 12.0, ^3J = 4.5), 3.62 (dd, ^3J = 9.0, 8.8), 3.13 (dd, ^2J = 12.0, ^3J = 10.5), 2.08 (3 H, s), 1.87−1.80 (2 H, m), 1.49 (9 H, s), 1.32 (3 H, s), 0.89 (9 H, s), 0.12, 0.08 (2 × 3 H, 2s).

10,11-Anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-7-*C*-methylidene-9-*O*-(methoxymethyl)-β-L-*xylo*-L-*ido*-undecofuranose (59). A mixture of **54** (153 mg, 0.176 mmol), anhydrous DMF (1.5 mL), and CsF (107 mg, 0.7 mmol) was stirred at 20 °C for 18 h. The solvent was evaporated. FC (15 g SiO_2, CH_2Cl_2/MeOH 95:5) gave 55 mg (83%) of a yellowish oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.89 (d, ^3J = 4.0), 5.33, 5.27 (2 H, 2s), 4.86, 4.74 (2d, ^2J = 6.5), 4.55 (d, ^3J = 4.0), 4.45 (dd, ^3J = 9.0, 2.5), 4.39 (d, ^3J = 5.5), 4.32 (ddd, ^3J = 8.5, 6.0, 2.5), 4.18 (d, ^3J = 2.5), 3.55 (dd, ^3J = 6.5, 5.5), 3.41 (3 H, s), 3.14 (ddd, ^3J = 6.5, 4.5, 3.0), 2.80 (dd, ^2J = 5.0, ^3J = 4.5), 2.66 (dd, ^2J = 5.0, ^3J = 3.0), 2.11 (ddd, ^2J = 14.0, ^3J = 6.0, 2.5), 1.98 (ddd, ^2J = 14.0, ^3J = 9.0, 8.5), 1.49, 1.31 (2 × 3 H, 2s).

6,11-Anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-7-*C*-methylidene-9-*O*-(methoxymethyl)-β-L-*xylo*-L-*ido*-undecofuranose (60). A mixture of **59** (15 mg, 0.040 mmol), anhydrous MeOH (0.4 mL), and K_2CO_3 (11 mg, 0.08 mmol) was stirred at 50 °C for 1 h. The solvent was evaporated under reduced pressure. FC (CH_2Cl_2/MeOH 95:5) gave 12 mg (80%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (d, ^3J = 4.0), 5.58, 5.23 (2 H, 2 br s), 4.91, 4.83 (2 H, 2d, ^2J = 7.0), 4.56 (d, ^3J = 4.0), 4.32 (ddd, ^3J = 9.0, 6.0, 2.5), 4.29 (dd, ^3J = 10.5, ^3J = 2.5), 4.27 (d, ^3J = 9.5), 4.13 (d, ^3J = 2.5), 3.87 (dd, ^2J = 12.5, ^3J = 4.5), 3.62 (ddd, ^3J = 11.0, 7.5, 4.5), 3.51 (3 H, s), 3.27 (dd, ^2J = 12.5, ^3J = 11.0), 3.03 (dd, ^3J = 9.5, 7.5), 2.09 (ddd, ^2J= 14.5, ^3J = 10.5, 9.0), 1.97 (ddd, ^2J = 14.5, ^3J = 6.0, 2.5), 1.51, 1.32 (2 × 3 H, 2s).

3,8,10-Tri-*O*-acetyl-6,11-anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-7-*C*-methylidene-9-*O*-(methoxymethyl)-β-L-*xylo*-L-*ido*-undecofuranose (61). Same procedure as for the preparation of **58**, starting with **60** (7 mg, 0.018 mmol): yield 8 mg (85%) of a colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88 (d, ^3J = 4.0), 5.33, 5.19 (2 H, 2s), 5.31 (d, ^3J = 9.5), 5.13 (d, ^3J = 3.0), 4.92 (ddd, ^3J = 10.5, 8.5, 4.5), 4.83, 4.70 (2d, ^2J = 7.0), 4.52 (1 H, m), 4.50 (d, ^3J = 4.0), 4.29 (dd, ^3J = 11.0, 3.0), 4.76 (dd, ^2J = 12.0, ^3J = 4.5), 3.63 (dd, ^3J = 9.5, 8.5), 3.36 (3 H, s), 3.24 (dd, ^2J = 12.0, ^3J = 10.5), 2.11 (4 H, s + m), 2.10, 2.06 (2 × 3 H, 2s), 1.76 (ddd, ^2J = 14.5, ^3J = 9.0, 3.0), 1.52, 1.31 (2 × 3 H, 2s).

(7*R* or 7*S*)-10,11-Anhydro-5-deoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-β-L-*xylo*-L-*ido*-7-undeculofuranose-(1,4)-pyranose-(7,3) ((−)-62). 3% O_3 in O_2 was bubbled through a solution of **59** (17 mg, 0.045 mmol) in CH_2Cl_2 (0.8 mL) cooled to −65 °C. After persistence of the blue color, Me_2S (20 μL) was added slowly and the mixture was stirred at 20 °C for 1 h. CH_2Cl_2 (8 mL) was added and the solution was washed with brine (5 mL). The aqueous phase was extracted with CH_2Cl_2 (5 mL, twice). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (5 g SiO_2, CH_2Cl_2/MeOH 95:5) gave 10 mg (58%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.84 (d, ^3J = 4.0), 5.46, 4.79 (2d, ^2J = 6.5), 4.46 (d, ^3J = 4.0), 4.35 (ddd, ^3J = 3.5, 3.0, 2.0), 4.24 (d, ^3J = 2.0), 3.90 (dd, ^3J = 11.0, 5.0), 3.82 (d, ^3J = 2.0), 3.80 (dd, ^3J = 7.5, 2.0), 3.47 (3 H, s), 3.33 (ddd, ^3J = 7.5, 4.0, 3.0), 2.84 (dd, ^2J = 4.5, ^3J = 4.0), 2.59 (dd, ^2J = 4.5, ^3J = 3.0), 2.26 (ddd, ^2J = 14.5, ^3J = 5.0, 3.0), 1.97 (ddd, ^2J = 14.5, ^3J = 11.0, 3.5), 1.48, 1.30 (2 × 3 H, 2s); $[\alpha]^{25}_D$ = −16.1 (*c* = 0.61, $CHCl_3$).

(7*R* or 7*S*)-7,10-Anhydro-6,8,11-tri-*O*-acetyl-7-deoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-α-D-*arabino*-L-*ido*-7-undeculofuranose-(1,4)-pyranose-(7,3) (63). A mixture of (−)-**62** (10 mg, 0.026 mmol), anhydrous CH_2Cl_2 (0.2 mL), and camphorsulfonic acid (6 mg, 0.026 mmol) was stirred at 0 °C for 5 h. Et_3N (13 μL, 0.09 mmol) was added, and the mixture was stirred at 0 °C for 5 min. CH_2Cl_2 (5 mL) was added, and the solution was washed with brine (5 mL). The aqueous phase was extracted with CH_2Cl_2 (5 mL, twice). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. FC (10 g SiO_2, CH_2Cl_2/MeOH 95:5) gave 4 mg of a colorless oil. The product was dissolved in THF (50 μL), Ac_2O (25 μL), and pyridine (25 μL). 4-(Dimethylamino)-pyridine (1 mg) was added, and the mixture was stirred at 20 °C for 2 h. The solvent was evaporated under reduced pressure. FC (10 g SiO_2, Et_2O/light petroleum 3:1) gave 6 mg of a colorless oil of >90% purity: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.90 (d, ^3J = 4.0), 5.36 (d, ^3J = 6.0), 5.03 (dd, ^3J = 11.5, 5.5), 4.65, 4.58 (2d, ^2J = 7.0), 4.57 (d, ^3J = 4.0), 4.50 (dd, ^2J = 8.5, ^3J = 2.0), 4.34 (1 H, m), 4.23 (d, ^3J = 2.0), 4.20 (ddd, ^3J = 8.5, 5.5, 2.0), 4.15 (dd, ^2J = 8.5, ^3J = 5.5), 3.89 (dd, ^3J = 8.5, 6.0), 3.32 (3 H, s), 2.25 (ddd, ^2J = 14.0, ^3J = 5.5, 2.5), 2.12, 2.08 (2 × 3 H, 2s), 2.03 (4 H, m), 1.48, 1.31 (2 × 3 H, 2s).

3-*O*-(*tert*-Butyldimethylsilyl)-10-chloro-5,7,10-trideoxy-6,8,11-tri-*O*-(triethylsilyl)-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-[[(2-nitrophenyl)seleno]methyl]-α-D-*gluco*-L-*ido*-undecofuranose ((+)-64). Bu_3P (65 μL, 0.22 mmol) was added dropwise to a stirred solution of (+)-**53** (100 mg, 0.11 mmol), anhydrous THF (0.6 mL), and 2-nitrobenzeneselenyl cyanide (51 mg, 0.22 mmol). After stirring at 50 °C for 1 h (TLC, EtOAc/light petroleum 1:16, R_f (**53**) = 0.22, R_f (**64**) = 0.31) the solvent was evaporated under reduced pressure. FC (10 g SiO_2, EtOAc/light petroleum 1:16) gave 93 mg (76%) of a yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.27 (dd, ^3J = 8.5, ^4J = 1.5), 7.51 (dd, ^3J = 8.0, ^4J = 1.0), 7.49 (ddd, ^3J = 8.0, 7.5, ^4J = 1.5), 7.26 (ddd, ^3J = 8.5, 7.5, ^4J = 1.0), 5.85 (d, ^3J = 4.0), 4.81, 4.70 (2d, ^2J = 6.0), 4.33 (d, ^3J = 4.0), 4.29 (dd, ^3J = 8.5, 1.5), 4.27−4.15 (2 H, m), 4.06−3.92 (4 H, m), 3.99 (d, ^3J = 2.5), 3.34 (3 H, s), 3.26 (dd, ^2J = 11.5, ^3J = 3.5), 2.97 (dd, ^2J = 11.5, ^3J = 7.0), 2.42 (1 H, m), 1.93 (ddd, ^2J = 14.5, ^3J = 10.5, 4.0), 1.71 (ddd, ^2J = 14.5, ^3J = 8.5, 1.5), 1.47, 1.30 (2 × 3 H, 2s), 1.01−0.91 (27 H, m), 0.86 (9 H, s), 0.72−0.61 (18 H, m), 0.11, 0.05 (2 × 3 H, 2s); $[\alpha]^{25}_D$ = +22.7 (*c* = 1.2, $CHCl_3$).

10,11-Anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-[[(2-nitrophenyl)seleno]methyl]-β-L-*ido*-L-*ido*-undecofuranose ((−)-65). A mixture of (+)-**64** (220 mg, 0.21 mmol), anhydrous DMF (2.2 mL), and CsF (125 mg, 0.8 mmol) was stirred at 20 °C for 24 h. The solvent was evaporated under reduced pressure. FC (30 g SiO_2, CH_2Cl_2/MeOH 95:5) gave 96 mg (78%) of a yellow solid: mp 48−51 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.28 (d, ^3J = 8.0), 7.57 (2 H, m), 7.33 (ddd, ^3J = 8.0, 5.5, ^4J = 3.0), 5.89 (d, ^3J = 4.0), 4.86, 4.75 (2d, ^2J = 6.5), 4.56 (d, ^3J = 4.0), 4.30 (ddd, ^3J = 6.5, 6.0, 2.5), 4.20 (1 H, m), 4.18 (d, ^3J = 2.5), 4.05 (dd, ^3J = 6.0, 3.5), 3.58 (dd, ^3J = 6.5, 6.0), 3.42 (3 H, s), 3.20−3.13 (2 H, m), 3.06 (dd, ^2J = 12.0, ^3J = 5.0), 2.83 (dd, ^2J = 4.5, ^3J = 4.0), 2.74 (dd, ^2J = 4.5, ^3J = 2.5), 2.07−1.99 (3 H, m), 1.49, 1.30 (2 × 3 H, 2s); $[\alpha]^{25}_D$ = −30.1 (*c* = 0.61, $CHCl_3$).

3,6,8-Tri-*O*-acetyl-10,11-anhydro-5,7-dideoxy-1,2-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-[[(2-nitrophenyl)-seleno]methyl]-β-L-*ido*-L-*ido*-undecofuranose (68), 3,8,11-tri-*O*-acetyl-6,10-anhydro-5,7-dideoxy-1,2-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-[[(2-nitrophenyl)seleno]methyl]-α-D-*gluco*-L-*ido*-undecofuranose (69), and 3,6,10-tri-*O*-acetyl-8,11-anhydro-5,7-dideoxy-*O*-1,2-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-[[(2-nitrophenyl)seleno]methyl]-β-L-*ido*-L-*ido*-undecofuranose (72). A mixture of (−)-**65** (78 mg, 0.13 mmol), anhydrous CH_2Cl_2 (0.78 mL), and camphorsulfonic acid (30 mg, 0.13 mmol) was stirred at 0 °C for 18 h. Et_3N (64 μL) was added, and the mixture was stirred at 0 °C for 5 min. The solvent was evaporated under reduced pressure. FC (15 g SiO_2, CH_2Cl_2/MeOH 95:5, R_f (**66**) = R_f (**65**) = 0.24, R_f (**67**) = 0.17) gave an initial fraction of 46 mg of a 2:1 mixture of **66** and (−)-**65**. A second fraction gave 7 mg (14%) of **67**. The first fraction was dissolved in THF (0.1 mL), Ac_2O

(50 μL), pyridine (50 μL), and 4-(dimethylamino)pyridine (1.6 mg). After stirring at 20 °C for 3 h the solvent was evaporated under reduced pressure. FC (15 g SiO_2, Et_2O/light petroleum 8:1, R_f (**69**) = 0.24, R_f (**68**) = 0.20) gave a first fraction of 20 mg (22% based on (−)-**65**) of **69**. A second fraction provided 15 mg (16%) of **68**. The fraction containing **67** (7 mg) was acetylated as above to give 7 mg (11%, based on (−)-**65**) of **72**.

Data for 68: orange oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.27 (dd, ^3J = 8.5, ^4J = 1.5), 7.58−7.55 (2 H, m), 7.34 (ddd, ^3J = 8.5, 6.5, ^4J = 1.5), 5.83 (d, ^3J = 4.0), 5.25 (ddd, ^3J = 8.0, 4.0, 3.0), 5.23 (dd, ^3J = 7.5, 3.5), 5.08 (d, ^3J = 3.0), 4.86, 4.72 (2d, ^2J = 6.5), 4.47 (d, ^3J = 4.0), 4.26 (ddd, ^3J = 8.5, 5.0, 3.0), 3.66 (dd, ^3J = 6.5, 3.5), 3.40 (3 H, s), 3.00 (2 H, m), 2.95 (ddd, ^3J = 6.5, 4.0, 2.5), 2.73 (dd, ^2J = 4.5, ^3J = 4.0), 2.59 (dd, ^2J = 4.5, 2.5), 2.10, (6 H, s), 2.08 (6 H, s), 2.10−1.91 (3 H, m), 1.46, 1.28 (2 × 3 H, 2s).

Data for 69: yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.30 (dd, ^3J = 8.0, ^4J = 1.5), 7.55 (ddd, ^3J = 8.0, 7.0, ^4J = 1.5), 7.45 (dd, ^3J = 8.0, ^4J = 1.0), 7.35 (ddd, ^3J = 8.0, 7.0, ^4J = 1.0), 5.87 (d, ^3J = 4.0), 5.24 (dd, ^3J = 9.5, 7.5), 5.14 (d, ^3J = 3.0), 4.71, 4.58 (2d, ^2J = 7.0), 4.54 (d, ^3J = 4.0), 4.43 (ddd, ^3J = 8.0, 4.0, 3.0), 4.35 (ddd, ^3J = 11.0, 5.5, 3.0), 4.29 (dd, ^2J = 12.0, ^3J = 5.5), 4.22 (dd, ^2J = 12.0, ^3J = 3.0), 3.76 (ddd, ^3J = 8.0, 5.5, 3.0), 3.53 (dd, ^3J = 8.0, 7.5), 3.35 (3 H, s), 2.99 (dd, ^2J = 12.0, ^3J = 7.5), 2.81 (dd, ^2J = 12.0, ^3J = 7.0), 2.33 (dddd, ^3J= 9.5, 7.5, 7.0, 5.5), 2.17, 2.14, 2.11 (3 × 3 H, 3s), 2.15−2.09 (1 H, m), 1.81 (ddd, ^2J = 14.5, ^3J = 8.0, 3.0), 1.52, 1.31 (2 × 3 H, 2s).

3,8,11-Tri-*O*-acetyl-6,10-anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-methylidene-α-D-*arabino*-L-*ido*-undecofuranose ((+)-70). mCPBA (19.6 mg, 0.062 mmol, 55%, Fluka No 25800) was added to a stirred solution of **69** (20 mg, 0.028 mmol) in CH_2Cl_2 (0.3 mL) and a saturated aqueous solution of $NaHCO_3$ (0.1 mL) cooled to 0 °C. The mixture was then stirred at 20 °C for 20 min (TLC, Et_2O/light petroleum 8:1, R_f (**69**) = 0.24, R_f (**70**) = 0.42). H_2O (5 mL) and CH_2Cl_2 (7 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (5 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (Et_2O/light petroleum 3:1) gave 13 mg (91%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88 (d, ^3J = 4.0), 5.56 (ddd, ^3J = 8.0, ^4J = 1.5, 1.0), 5.13 (d, ^3J = 3.0), 5.08 (br s), 4.98 (d, ^4J = 1.5), 4.74, 4.61 (2d, ^2J = 7.0), 4.60 (dd, ^3J = 11.0, 3.5), 4.52 (d, ^3J = 4.0), 4.44 (ddd, ^3J = 8.5, 4.0, 3.0), 4.27 (d, ^3J = 5.0), 4.26 (d, ^3J = 3.0), 3.83 (ddd, ^3J = 8.5, 5.0, 3.0), 3.58 (dd, ^3J = 8.5, 8.0), 3.36 (3 H, s), 2.20 (ddd, ^2J = 14.5, ^3J = 11.0, 4.0), 2.17, 2.12, 2.10 (3 × 3 H, 3s), 1.82 (ddd, ^2J = 14.5, ^3J = 8.5, 3.5), 1.52, 1.31 (2 × 3 H, 2s); $[\alpha]^{25}_D$ = +34.4 (*c* = 0.95, $CHCl_3$).

3,8,11-Tri-*O*-acetyl-6,10-anhydro-5-deoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-α-D-*arabino*-L-*ido*-7-undeculofuranose ((+)-71). O_3 (3% in O_2) was bubbled through a solution of (+)-**70** (15 mg, 0.030 mmol) in CH_2Cl_2 (1 mL) cooled to −78 °C. After persistence of the blue color, Me_2S (27 μL, 0.3 mmol) was added slowly, and the mixture was stirred at 20 °C for 1 h. The solvent was evaporated yielding 17 mg of a white solid which could be recrystallized from toluene at −20 °C to give 12 mg (80%) of white crystals: mp 117−118.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.86 (d, ^3J = 4.0), 5.58 (d, ^3J = 10.0), 5.13 (d, ^3J = 3.0), 4.74, 4.62 (2d, ^2J = 7.0), 4.51 (d, ^3J = 4.0), 4.44 (ddd, ^3J = 9.0, 4.0, 3.0), 4.40 (dd, ^3J= 11.0, 3.5), 4.34 (d, ^3J = 3.5), 4.33 (d, ^3J = 5.0), 4.16 (ddd, ^3J = 7.5, 5.0, 3.5), 3.97 (dd, ^3J = 10.0, 7.5), 3.37 (3 H, s), 2.20, 2.11, 2.10 (3 × 3 H, 3s), 2.03 (ddd, ^2J = 14.5, ^3J = 9.0, 3.5), 1.91 (ddd, ^2J = 14.5, ^3J = 11.0, 4.0), 1.51, 1.30 (2 × 3 H, 2 s). $[\alpha]^{25}_D$ = +54.6 (*c* = 0.85, $CHCl_3$).

3,6,10-Tri-*O*-acetyl-8,11-anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-methylidene-β-L-*xylo*-L-*ido*-undecofuranose (73). mCPBA (19.6 mg, 55%) was added portionwise to a stirred solution of **72** (20 mg, 0.028 mmol) in CH_2Cl_2 (210 μL) and a saturated aqueous solution of $NaHCO_3$ (70 μL) cooled to 0 °C. After stirring at 20 °C for 30 min, CH_2Cl_2 (5 mL) and a saturated aqueous solution of $NaHCO_3$ (5 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (5 mL, three times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (Et_2O/light petroleum 3:1) gave 8 mg (56%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.87 (d, ^3J = 4.0), 5.44, 5.38 (2 br s), 5.43 (br d, ^3J = 9.5), 5.25 (ddd, ^3J = 4.5, 1.5, 1.0), 5.16 (d, ^3J = 3.0), 4.70, 4.63 (2d, ^2J = 7.0), 4.57 (br d, ^3J = 3.5), 4.49 (d, ^3J = 4.0), 4.31 (dd, ^2J = 10.5, ^3J = 4.5), 4.28 (1 H, m), 4.14 (br d, ^3J = 3.5), 3.80 (dd, ^2J = 10.5, ^3J = 1.5), 3.33 (3 H, s), 2.12, 2.11, 2.05 (3 × 3 H, 3s, 2 H, m), 1.49, 1.30 (2 × 3 H, 2s); $[\alpha]^{25}_D$ = +1 (*c* = 0.50, $CHCl_3$).

6,10-Anhydro-5,7-dideoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-7-*C*-methylidene-α-D-*arabino*-L-*ido*-undecofuranose ((−)-74). A mixture of (−)-**65** (50 mg, 0.086 mmol), anhydrous CH_2Cl_2 (0.5 mL), and camphorsulfonic acid (20 mg, 0.086 mmol) was stirred at 0 °C for 18 h. Et_3N (42 μL, 0.30 mmol) was added, and the mixture stirred at 0 °C for 5 min. The solvent was evaporated. FC (15 g SiO_2, CH_2Cl_2/MeOH 95:5, R_f (**66**) = 0.24, R_f (**67**) = 0.17) gave a first fraction of 32 mg composed of a 2:1 mixture of **66** and (−)-**65**, and a second fraction containing 7 mg (14%) of **67**. The first fraction was dissolved in anhydrous CH_2Cl_2 (0.3 mL) and cooled to 0 °C and mCPBA (85%, 12.3 mg) was added. After stirring at 0 °C for 20 min, Et_2NH (20 μL) was added and the mixture was stirred at 20 °C for 30 min. The solvent was evaporated and FC (10 g SiO_2, Et_2O/CH_2Cl_2/light petroleum 9.5/9.5/1, R_f (**74**) = 0.21, R_f (**59**) = 0.15) gave 7 mg (22% based on (−)-**65**) of (−)-**74** as a colorless oil, and 4 mg of **59**.

Data for (−)-74: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.89 (d, ^3J = 4.0), 5.33 (dd, ^2J = 1.5, ^4J = 2.0), 5.08 (dd, ^2J = 1.5, ^4J = 2.0), 4.78, 4.69 (2d, ^2J = 7.0), 4.54 (d, ^3J = 4.0), 4.52 (dd, ^3J = 11.0, 3.0), 4.47 (d, ^3J = 1.9), 4.30 (br d, ^3J = 9.5, ^4J = 2.0, ^3J = 1.9), 4.23 (ddd, ^3J = 8.5, 5.5, 3.0), 4.19 (br s), 3.88 (2 H, m), 3.68 (dd, ^2J = 11.0, ^3J = 6.5), 3.49 (3 H, s), 3.17 (dd, ^3J = 9.5, 9.0), 2.46 (ddd, ^2J = 14.5, ^3J = 11.0, 8.5), 1.84 (ddd, ^2J = 14.5, ^3J = 5.5, 3.0), 1.51, 1.32 (2 × 3 H, 2s); $[\alpha]^{25}_D$ = −20.8 (*c* = 0.84, $CHCl_3$).

(7*R*)- and (7*S*)-6,10-Anhydro-5-deoxy-1,2-*O*-isopropylidene-9-*O*-(methoxymethyl)-α-D-*arabino*-L-*ido*-7-undeculofuranose-(1,4)-pyranose-(7,3) ((+)-75). 3% O_3 in O_2 was bubbled through a solution of (−)-**74** (23 mg, 0.061 mmol) in CH_2Cl_2 (1 mL) cooled to −78 °C. After persistence of the blue color, Me_2S (53 μL) was added slowly and the mixture was stirred at 20 °C for 1 h. The solvent was evaporated to give 20 mg (85%) of a yellowish oil composed of a 2:1 mixture of anomeric 7-undeculoses: ^{13}C NMR (100.61 MHz, $CDCl_3$) of the major isomer δ 111.5 (s, Me_2C), 104.9 (d, ^1J(C,H) = 184, C(1)), 98.2 (t, ^1J(C,H) = 165, $MeOCH_2O$), 92.5 (s), 84.2 (d, ^1J(C,H) = 161, C(7)), 80.2 (d, ^1J(C,H) = 145), 76.4 (d, ^1J(C,H) = 154), 75.6 (d, ^1J(C,H) = 148), 74.7 (d, ^1J(C,H) = 153), 71.7 (d, ^1J(C,H) = 143), 70.0 (d, ^1J(C,H) = 152, C(2), C(3), C(4), C(6), C(8), C(9), C(10)), 61.5 (t, ^1J(C,H) = 143, C(11)), 56.1 (q, ^1J(C,H) = 142, MeO), 26.5, 26.0 (2q, ^1J(C,H) = 127, Me_2C), 24.6 (t, ^1J(C,H) = 135, C(5)); ^{13}C NMR (100.61 MHz, $CDCl_3$) of minor isomer δ 111.4 (s, Me_2C), 104.7 (d, ^1J(C,H) = 184, C(1)), 95.4 (t, ^1J(C,H) = 165, $MeOCH_2O$), 92.7 (s, C(7)), 84.0 (d, ^1J(C,H) = 161), 77.8 (d, ^1J(C,H) = 148), 76.4 (d, ^1J(C,H) = 154), 75.0 (d, ^1J(C,H) = 153), 73.8 (d, ^1J(C,H) = 146), 69.7 (d, ^1J(C,H) = 151), 67.6 (d, ^1J(C,H) = 143, C(2), C(3), C(4), C(6), C(8), C(9), C(10)), 61.6 (q, ^1J(C,H) = 140, MeO), 60.1 (t, ^1J(C,H) = 135, C(11)), 26.5, 26.1 (2q, ^1J(C,H) = 127, Me_2C), 25.2 (t, ^1J(C,H) = 131, C(5)); $[\alpha]^{25}_D$ = +22.2, $[\alpha]^{25}_{577}$ = +25.3, $[\alpha]^{25}_{546}$ = +28.8, $[\alpha]^{25}_{435}$ = +46.8, $[\alpha]^{25}_{405}$ = +53.9 (*c* = 0.90, $CHCl_3$).

Acknowledgment. We are grateful to the Swiss National Science Foundation, the Fonds Herbette (Lausanne) and F. Hoffmann-La Roche AG & Co. (Basel), for financial support.

Supporting Information Available: Spectral data and elemental analysis for various compounds (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO950285B