$\theta)/\lambda$. Non-hydrogen atoms were refined anisotropically. Positional parameters of all hydrogen atoms were refined with isotropic temperature factors. Occupancies of the two disordered CH_2OH substituents were fixed at 0.5 each, but no additional constraints were imposed.

Final refinements converged to the values of $R = \sum|\Delta F|/\sum|F_o| = 0.056$ and $R_w = [\sum w(DF)^2/\sum w|F_o|^2]^{1/2} = 0.070$ for all 2551 observations m and 260 variables n. The discrepancy factor $S = [\sum w(\Delta F)^2/(m-n)]^{1/2} = 0.86$. The largest final parameter shift observed was 0.01σ, and the largest peak on the final difference map was 0.4 e/Å^3. Atomic scattering factors for the non-hydrogen atoms were from ref 20. Scattering factors for the hydrogen atoms were those of Stewart et al.[21] The DNA system of programs was used throughout.[22] Final fractional atomic coordinates and thermal parameters are available as supplementary material.

Acknowledgment. We gratefully acknowledge Dr. Richard L. Cysyk and Ms. Nancy M. Malinowski of the Laboratory of Biological Chemistry, DTP, DCT, NCI, for the in vitro cytotoxicity data. We thank Dr. James A. Kelley, Laboratory of Medicinal Chemistry (LMC), for measuring the mass spectrum of neplanocin F and Dr. John S. Driscoll, Chief of the LMC, for his constant support and advice.

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, and bond lengths and angles (5 pages). This material is contained in many 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.

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Synthesis of α-(1→2)-, α-(1→3)-, α-(1→4)-, and α-(1→5)-C-Linked Disaccharides through 2,3,4,6-Tetra-*O*-acetylglucopyranosyl Radical Additions to 3-Methylidene-7-oxabicyclo[2.2.1]heptan-2-one Derivatives[1]

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Received June 4, 1991

The "naked sugar" (+)-1 (1*R*,2*S*,4*R*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*S'*)-camphanate) has been converted into (+)-(1*R*,4*R*,5*R*,6*R*)-3-methylidene-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**3**) and (−)-(1*S*,4*R*,5*R*,6*R*)-5-*exo*-(benzeneselenyl)-6-*endo*-chloro-3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one ((−)-**26**). Reductive addition of 2,3,4,6-tetra-*O*-acetylglucopyranosyl radical onto (+)-**3** and (−)-**26** were highly stereoselective giving exclusively 3-*endo*-(glucosylmethyl)-7-oxabicyclo[2.2.1]heptan-2-one derivatives. The anomeric selectivity (α-*C*-glucoside vs β-*C*-glucoside) was 5.5:1 with (+)-**3** and 8:1 with (−)-**26**. The *C*-glucosides so-obtained were transformed into α-(1→2)-, α-(1→3)-, α-(1→4)-, and α-(1→5)-C-linked disaccharide derivatives which combine α-D-glucopyranose with L-*altro*-hexonolactone, L-*manno*-hexonolactone, L-mannose, and L-(*talo*-hexofuranosid)uronic acid, respectively.

Introduction

The replacement of the interglycosidic oxygen atom in disaccharides by a methylene group generates a class of interesting analogues of disaccharides, namely the *C*-disaccharides, which constitute potential inhibitors of glycosidases[2a] and disaccharidases.[2b] Inhibitors of α-amylases and other mammalian intestinal carbohydrate-splitting enzymes have aroused medical interest in the treatment of metabolic diseases such as diabetes.[2b,3] Inhibitors of sucrose as well as maltase may bring about a reduction in food consumption and weight gain.[4] A large number of cellular recognition events are thought to involve the specific binding of particular classes of oligosaccharides on one cell surface to "receptor" glycoproteins on the surface of another cell.[5,6] The immense number of structures that can be made from a relatively small number of saccharide units and the multiplicity and specificity of the enzymes which assemble them suggest that intercellular communication is encoded in oligosaccharides.[5,7] Thus, specific glycosidase inhibitors may find applications as antiviral,[8] antitumor,[9] or fertility control agents.[10] Since

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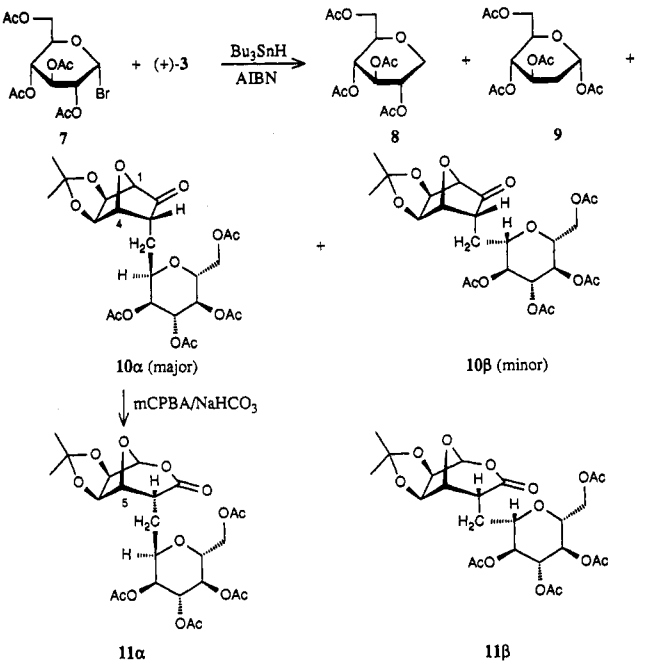
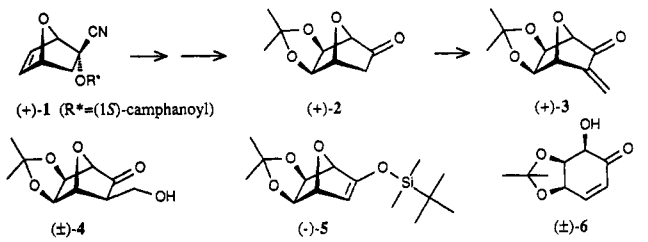
the first synthesis of a β-(1→6)-*C*-disaccharide (β-D-Glcp-C-(1→6)-α-D-Glcp-OMe) by Rouzaud and Sinay,[11] several approaches to C-disaccharides[12-19] and analogues[20-26] have been proposed.[27] Some of them rely on the condensation of an electrophilic and a nucleophilic reagent, both derived from a natural, protected carbohydrate[11-14,16,17,19-21,23,25] (see, e.g., the syntheses of methylene bridged analogues of maltose (α-D-Glc*p*-*C*-(1→4)-α-D-Glc*p*-OMe),[12a] cellobiose (β-D-Glc*p*-*C*-(1→4)-α-D-Glc*p*-OMe),[12a] sucrose (α-D-Glc*p*-*C*-(1→2)-β-D-Fru*f*), β,β-trehalose (β-D-Glc*p*-*C*-(1→1)-β-D-Glc*p*)[19]), others developed by Giese and co-workers are based on the addition of glycosyl radicals to α-methylene lactones derived from a carbohydrate, leading to α-(1→2)-*C*-disaccharides such as methylene-bridged analogues of kojibiose (α-D-Glc*p*-*C*-(1→2)-D-Glc) or ristobiose (α-D-Man*p*-*C*-(1→2)-D-Glc)[15] to α-D-Glc*p*-*C*-(1→2)-β-D-Rib*f*[10] and to α-L-Fuc*p*-*C*-(1→2)-α-D-Gal.[15] The method based on radical addition to olefin has been applied recently to the synthesis of a difluoromethylene bridged (1→6)-disaccharide (α-D-Gul*f*-CF_2-(1→6)-D-Glc*p*).[26] Danishefsky et al.[22] have applied the hetero-Diels–Alder addition to prepare long-chain carbohydrates and derivatives, including *C*-disaccharide analogues. Dawson et al.[24] have prepared the carbonyl-bridged disaccharides β-D-Xyl*p*-(CO)-(1→3)-D-Man*p*-OEt and β-D-Xyl*p*-(CO)-(1→2)-D-Glc*p*-OEt using the cycloaddition of a nitrile oxide derived from a carbohydrate to ethyl 4,6-*O*-diacetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside. Many of these approaches suffer from insufficient stereoselectivity and require chromatographic separation of stereomers. We have found that the additions of tetra-*O*-acetyl-D-glucopyranosyl radical to 3-methylene-7-oxabicyclo[2.2.1]heptan-2-one systems are highly stereoselective and give mostly α-D-glucopyranosyl-*C*-(1→3-*endo*)-7-oxabicyclo[2.2.1]heptan-2-one derivatives which can be converted into (1→2)-, (1→3)-, (1→4)- or (1→5)-*C*-disaccharides with high stereoselectivity.[27]

Scheme I



Results and Discussion

The "naked sugar" 1 (Diels–Alder adduct of furan to 1-cyanovinyl (1*S*)-camphanate)[28] was converted to the 7-oxabicyclo[2.2.1]heptan-2-one derivative (+)-2 following a procedure already described.[29] Treatment of (+)-2 with



monomeric formaldehyde and *N*-methylanilinium trifluoroacetate[30] led to the expected α-methylene ketone (+)-3. Acceptable on small-scale preparations (0.1 g, 57%), the yield of that reaction did not surpass 35% on multigram scale. Quenching the potassium enolate of (±)-2 (prepared with $(Me_3Si)_2NK$ in THF) with monomeric CH_2O[31] at −78 °C afforded aldol (±)-4 in 40% yield only. We finally found that (+)-3 could be obtained on a multigram scale in a reproducible fashion (53%) on condensing the Eschenmoser's salt (CH_2=NMe_2I) onto the silyl enol ether (−)-5 (derived from (+)-2[32]) in the presence of 1 equiv of hexamethylphosphoric triamide (HMPT).[33] Attempts

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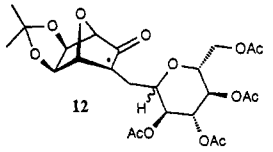
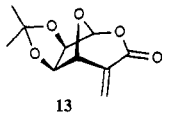
to add enol ether (±)-5 onto carbon electrophilic agents such as $ClCH_2SPh/TiCl_4$, $ICH_2SPh/ZnBr_2$,[34] or $ClCOOEt/TiCl_4$ failed to give the expected products of alkylation and led to various mixtures containing the ketone (±)-2, enone (±)-6 (resulting from the 7-oxa bridge opening[35]), and products of decomposition.

Under conditions similar to those recommended by Giese et al.,[10] the slow addition of Bu_3SnH and AIBN (catalyst) in toluene to a boiling solution of (+)-3 and α-acetobromoglucose (7; 1.3 equiv) in toluene afforded a mixture of the deoxy-D-glucose derivatives 8 + 9 (37%) and the product of reductive addition (+)-10. The *C*-glucoside (+)-10 could be separated from 8 + 9 by column chromatography. It consisted of a 5.5:1 mixture of the *C*-D-glucosyl α- and β-anomer 10α and 10β, respectively. Baeyer–Villiger oxidation of (+)-10 with *m*-chloroperbenzoic acid (mCPBA) and $NaHCO_3$ led to (+)-11 (96.5%), a mixture of the corresponding uronolactones 11α and 11β. The endo configuration of the (2′,3′,4′,6′-tetra-*O*-acetyl-D-glucopyranosyl)methyl substituent at the α position of the ketone moiety in (+)-10 and of the lactone moiety in (+)-11 was given by the vicinal coupling constant of ca. 5 Hz measured between H-C(3) and H-C(4) in (+)-10 and between H-C(4) and H-C(5) in (+)-11.[36] No trace of the 3-exo-isomer of (+)-10 could be detected in the 360-MHz ^1H NMR spectrum of the crude reaction mixture, thus demonstrating the high stereoselectivity of the reductive D-glucopyranosyl radical addition to the bicyclic enone (+)-3. This result can be interpreted in terms of the formation of the 7-oxabicyclo[2.2.1]heptyl radical intermediate 12 whose reaction with Bu_3SnH is expected to be highly exo face selective.[37] When $(Me_3Si)_3SiH$[38] was used instead of Bu_3SnH as hydrogen atom donor,[18] the yield in 10α + 10β never surpassed 28%.



12



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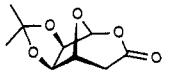
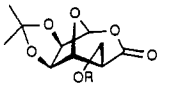


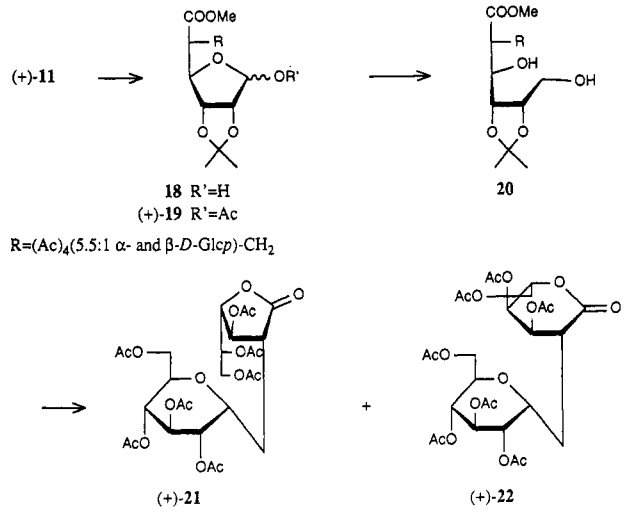
14



15 R=Bn
16 R=H
17 R=Ms

Radical glycosidation of α-methylene lactone 13 with 7 and Bu_3SnH/AIBN led to 73% yield of a 5.5:1 mixture of 11α and 11β (mixtures of diastereomers as racemic 13 was used). Compound 13 was prepared in the following way. Lactone 14 derived from (±)-2[29] was deprotonated with $(Me_3Si)_2NLi$ and the corresponding enolate treated with $PhCH_2OCH_2Br$ to give 15 (70%). Debenzylation (H_2/Pd–C) afforded the corresponding alcohol 16 (>98%)

Scheme II



which was esterified at 0 °C with CH_3SO_2Cl in pyridine into 17. At 20 °C and in pyridine, 17 eliminated CH_3SO_3H and afforded 13 (95%). Alcaline methanolysis of 11α + 11β followed by acetylation (Ac_2O/pyridine/DMAP) gave the [5-deoxy-5-(D-*gluco*-pyranosyl)methyl-L-*talo*-hexofuranosyl]uronate (+)-19 (90%). When the methanolysis of (+)-11 was followed by reduction with $NaBH_4$, the diol 20 was formed. Treatment with 1 N HCl (40 °C) and then with Ac_2O/pyridine/DMAP led to a mixture of hexono-1,4- and hexono-1,5-lactones from which (+)-21 and (+)-22 (Scheme II) could be isolated pure by column chromatography on silica gel in 36 and 31% yield, respectively. Thus, the Giese's method of radical glycosidation applied to α-methylene ketone (+)-3 or to α-methylene lactone 13 derived from the naked sugar (+)-1 allowed one to prepare 5.5:1 mixtures of α- and β-D-Glc*p*-*C*-(1→5)-αβ-L-(*talo*-hexofuranosyl)uronate derivatives 18 and (+)-19 and α-D-Glc*p*-*C*-(1→2)-L-*altro*-hexono-1,4- and -1,5-lactone derivatives (+)-21, (+)-22. We show below how the same approach can be applied to the synthesis of α-D-Glc*p*-(1→3)- and α-D-Glc*p*-(1→4)-*C*-L-mannose derivatives.

Under kinetically controlled conditions, the reaction of benzeneselenyl chloride with (+)-7-oxabicyclo[2.2.1]-hept-5-en-2-one ((+)-23) derived from (+)-1 gave adduct (+)-24 nearly quantitatively.[40] The high regioselectivity of this electrophilic addition has been attributed to the electron-releasing effect of the homoconjugated carbonyl moiety due to favorable through-bond n(CO) ↔ σC(1), C(2) ↔ pC(6) interactions.[28,41] Treatment on the enol silyl ether (−)-25 derived from (+)-24[40b] with the Eschenmoser's salt ($H_2C{=}NMe_2I$) and HMPT afforded the α-methylene ketone (−)-26 (84%). When a solution of Bu_3SnH in benzene containing 5 mol % of AIBN was added slowly to a boiling solution of (−)-26 and 7 a mixture was obtained from which the α-*C*-glucoside (+)-27 (48.5%), the β-*C*-glucoside (+)-28 (6%), and the reduced glucose derivatives 8 + 9 were separated and isolated by column chromatography on silica gel (Scheme III). In this case, the "α/β anomer selectivity" at C(1′) of the glucopyranosyl unit was 8:1, which is slightly better than for the related glucosydations of (+)-3 and 13 (α/β 5.5:1) under similar conditions. Strickingly, no trace of products resulting from the reduction of the chloride or/and of the benzeneselenyl

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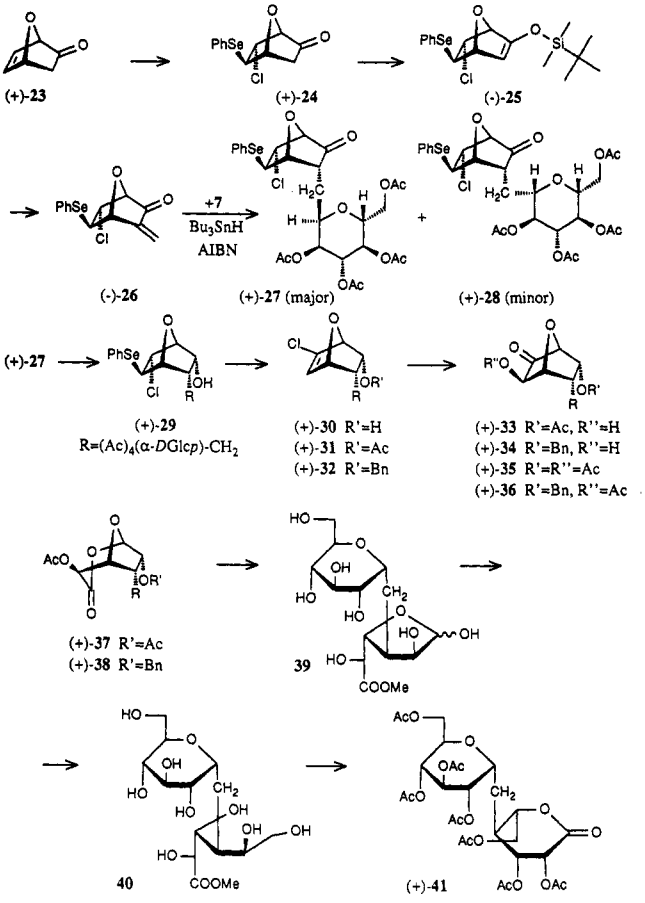
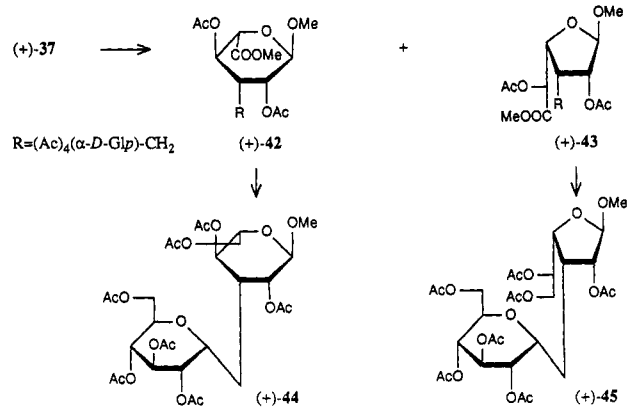
Scheme III



functions could be detected in the crude reaction mixture (360-MHz ^1H NMR). Furthermore, and as in the case of reaction (+)-**3** + **7**/Bu_3SnH (Scheme I), no trace of the C(3) exo stereomers of (+)-**27** and (+)-**28** could be seen, thus pointing out the high exo face selectivity of the hydrogen atom transfer from Bu_3SnH to the radical intermediate resulting from the addition of 2,3,4,6-tetra-*O*-acetylglucopyranosyl radical to enone (−)-**26**. The endo configuration of the glucosylmethyl substituents at C(3) in (+)-**27** and (+)-**28** was determined by the observations (double irradiation experiments) of a vicinal coupling constant of 6 Hz between H-C(3) and H-C(4) of the bicyclic system[36] and NOE measurements between H-C(5) and the CH_2–C(3) protons. The α-configuration of the "anomeric" center C(1′) of the *C*-glucoside was expected for the major product[13,15,18,42] and was confirmed by the vicinal coupling constant ^3J(Heq-C(1′),Hax-C(2′)) = 4 Hz[43] measured in the ^1H NMR spectrum of (+)-**27**. These features were also found in the ^1H NMR spectra of **10**α, **11**α, (+)-**19**, (+)-**21**, (+)-**22** and of the derivatives of (+)-**27** described herebelow (Schemes III and IV).

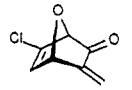
Reduction of ketone (+)-**27** with $NaBH_4$ furnished the expected endo alcohol (+)-**29** (96%). Oxidative elimination of the PhSe group with mCPBA gave the corresponding chloroalkenol (+)-**30** (96%) which was acetylated (Ac_2O/pyridine, DMAP) into (+)-**31** (97%) or benzylated (NaH/DMF, BnBr) into (+)-**32** (25%). Double hydroxylation of the chloroalkenes (+)-**31** and (+)-**32** gave the α-hydroxy ketones (+)-**33** (99%) and (+)-**34** (85%), respectively, which were acetylated (Ac_2O/pyridine/DMAP) into (+)-**35** (94%) and (+)-**36** (95%), respectively. Their Baeyer–Villiger oxidation with (mCPBA/$NaHCO_3$) led to the corresponding urono-6,1-lactones (+)-**34** (94%) and (+)-**38** (85%). Alcaline methanolysis (MeOH/K_2CO_3) of (+)-**37** gave methyl 4-deoxy-4-[(α-D-*gluco*-pyranosyl)-methyl]-L-α*β*-*manno*-furanouronate (**39**) which was reduced with $NaBH_4$ (MeOH) into the corresponding α-D-Glc-*C*-(1→4)-L-*manno*-hexonate **40**. Treatment with HCl and then with Ac_2O/pyridine/DMAP gave the peracetylated derivative (+)-**41** in 62% yield.

Scheme IV



Under acidic conditions, the methanolysis of uronolactone (+)-**37** (MeOH + $SOCl_2$)[43] gave a mixture of partially deprotected methyl uronates that was reacetylated with Ac_2O/pyridine/DMAP. Column chromatography on silica gel afforded the corresponding L-*manno*-hexopyranoside (+)-**42** (28%) and L-*manno*-hexofuranoside (+)-**43** (27%). $LiAlH_4$ reductions of (+)-**42** and (+)-**43** in tetrahydrofuran (THF), followed by acetylation (Ac_2O/pyridine/DMAP), afforded the fully protected (1→3)-*C*-disaccharides α-D-Glc*p*-*C*-(1→3)-*β*-L-Man*p*-OMe ((+)-**44**, 98%) and α-D-Glc*p*-*C*-(1→3)-*β*-L-Man*f*-OMe ((+)-**45**, 93%), respectively (Scheme IV).

The structures of the new compounds described here were all consistent with their elemental analyses, their spectral data (see Experimental Section), and their mode of formation. With the hope to improve the overall yield of our method of synthesis of C-(1→3) and C-(1→4) disaccharides we explored the possibility to use **46** as a



46

tetra-*O*-acetyl-D-glucopyranosyl radical scavenger. Dienone **46** was obtained in 60% yield by oxidative elimination (mCPBA) of the benzeneselenyl moiety in racemic (±)-**26**. Unfortunately, all our attempts to generate C-glucosidated compounds with **7** Bu_3SnH/AIBN and **46** led to products of C–C coupling with yields that never surpassed 20%.

Conclusion

Starting with the naked sugar (+)-**1** ((1*R*,2*S*,4*R*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*S*′)-camphanate)), α-(1→2)- (Scheme II), α-(1→3)- (Scheme IV), α-(1→4)- (Scheme III), and α-(1→5)-*C*-linked disaccharide derivatives (Scheme II) combining α-D-glucopyranose with L-*altro*-hexonolactone, L-*manno*-hexonolactone, L-mannose, and L-(*talo*-hexofuranosyl)uronic acid, respectively, have been prepared with good stereoselectivity. Using instead of (+)-**1** its diastereomer (1*S*,2*R*,4*S*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*R*′)-camphanate ((1*R*)-camphanic acid as chiral auxiliary instead of

(42) Korth, H.-G.; Sustmann, R.; Giese, B.; Rückert, B.; Gröninger, K. S. *Chem. Ber.* **1990**, *123*, 1891. Korth, H.-G.; Praly, J.-P.; Somsak, L.; Sustmann, R. *Ibid.* **1990**, *123*, 1155.
(43) Ferrari, T.; Vogel, P. *Synlett* **1991**, 233.

(1*S*)-camphanic acid),[28] our approach should allow one to prepare the corresponding *C*-D-glucosides of D-*altro*-hexonolactone, D-*manno*-hexonolactone, D-mannose, and (D-*altro*-hexofuranosyl)uronic acid. The α-methylene ketones (+)-**3** and (−)-**26** and their enantiomers are expected to add carbohydrate radicals other than 2,3,4,6-tetra-*O*-acetylglucopyranosyl and thus should make possible the preparation of a large variety of *C*-disaccharides.

Experimental Section

For general remarks, see ref 44. *J* values are given in Hz.

(+)-(1*R*,4*R*,5*R*,6*R*)-3-Methylidene-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((+)-3). Method A. A mixture of (+)-**2** (100 mg, 0.54 mmol),[29] *p*-formaldehyde (122 mg, 8 equiv), and *N*-methylanilinium trifluoroacetate (540 mg, 2.4 mmol) in anhydrous tetrahydrofuran (THF, 5 mL) was heated under reflux and under Ar atmosphere for 1.5 h. After the mixture was cooled to 10 °C, ether (5 mL) was added. The precipitate was filtered off and washed with Et_2O/CH_2Cl_2 (1:1) (10 mL, three times). The combined organic solutions were washed with a saturated aqueous solution of $NaHCO_3$ (20 mL) and then with brine (15 mL). After drying ($MgSO_4$), the solvent was evaporated and the residue filtered through a short column of silica gel (light petroleum/AcOEt (3:1)), yielding 56 mg (57%) of yellowish crystals: mp 100–102 °C. **Method B.** A mixture of (−)-**5** (100 mg, 0.33 mmol)[32] *N,N*-dimethylmethyleneimmonium iodide (93 mg, 0.5 mmol), hexamethylphosphoric triamide (HMPT, 64 μL, 0.33 mmol) and anhydrous THF was heated under reflux for 1.5 h. After the mixture was cooled to 20 °C, CH_2Cl_2 (10 mL) and then H_2O (10 mL) were added. Following the same workup procedure as above (method A), 35 mg (53%) of pure (+)-**3** was obtained: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.99 (d, J = 1.1), 5.47 (d, J = 1.1, $H_2C{=}C(3)$), 5.01 (d, J = 1, HC(1)), 4.52 (s, HC(5), HC(6)), 4.35 (d, ^4J = 1.0, HC(4)), 1.50, 1.30 (2 s, 2 Me); $[\alpha]^{25}_{589}$ = +11.3°, $[\alpha]^{25}_{578}$ = +12.1°, $[\alpha]^{25}_{546}$ = +16°, $[\alpha]^{25}_{436}$ = +27°, $[\alpha]^{25}_{365}$ = +29° (c = 27 g/dm^3, CH_2Cl_2); UV (MeOH) λ_{max} = 224 (ε 6720); UV (CH_3CN) 224 (7050), 370 (80).

(±)-(1*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-3-(Hydroxymethyl)-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((±)-4). Freshly prepared monomeric formaldehyde (3 mL) was added to a solution of (±)-**2** (1.22 g, 6.63 mmol) in anhydrous THF cooled to −78 °C. A freshly prepared solution of $(Me_3Si)_2NK$ (1.2 equiv) in THF was then added under vigorous stirring and Ar atmosphere. After being stirred at −78 °C for 40 min, the solution was allowed to warm to 0 °C and was neutralized (pH ≅ 7) with 1 N aqueous HCl. After the addition of a saturated aqueous solution of NH_4Cl, the mixture was extracted with AcOEt (100 mL, three times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (Lobar Column C, AcOEt/light petroleum (1:3)), yielding 260 mg of a product of aldolization of (±)-**2**, white solid, mp 210–212 °C, and 560 mg (40%) of (±)-**4** as colorless crystals: mp 38–40 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.72 (d, J = 1.5, HC(1)), 4.56–4.54 (2d, J = 5.5, HC(5), HC(6)), 4.30 (d, J = 1.5, HC(4)), 3.85 (m, $CH_2C(3)$), 2.12 (t, J = 7, HC(3)), 2.02 (s, OH), 1.50, 1.32 (2s, 2 Me).

Mixture of (1*R*,3*R*,4*R*,5*R*,6*R*)-3-*endo*-[(2′,3′,4′,6′-Tetra-*O*-acetyl-α- and -β-D-*gluco*-pyranosyl)methyl]-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one (10α/10β). A mixture of (+)-**3** (275 mg, 1.4 mmol), α-acetobromoglucose (Fluka, 748 mg, 1.82 mmol), and α,α′-azoisobutyronitrile (AIBN, 15 mg, 0.09 mmol) in anhydrous toluene (5 mL) was heated under reflux (appearance of a green color). A solution of Bu_3SnH (611 mg, 2.1 mmol) and AIBN (19 mg, 0.12 mmol) in anhydrous toluene (3 mL) was added slowly by means of a mechanical syringe (ca. 1 h). The solvent was evaporated under vacuum (0.05 Torr) and the residue filtered through a column of a silica gel (AcOEt). After solvent evaporation, the residue was purified by column chromatography on silica gel (Lobar, column B, light petroleum/AcOEt (1.5:1)). A first fraction gave 226 mg (0.68 mmol) of a mixture of 2,3,4,6-tetra-*O*-acetyl-1-deoxy-1,5-anhydroglucitol (**8**)[15b] and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose (**9**)[15b] (ratio 90:10). A second fraction yielded 504 mg (68%) of a 5.5:1 mixture of **10α** and **10β**, colorless solid: mp 142–143 °C (after recrystallization from AcOEt/light petroleum); $[\alpha]^{25}_{589}$ = +46°, $[\alpha]^{25}_{578}$ = +48°, $[\alpha]^{25}_{546}$ = +55°, $[\alpha]^{25}_{436}$ = +102°, $[\alpha]^{25}_{365}$ = +140° (c = 15 g/dm^3, CH_2Cl_2); ^{1}H NMR (360 MHz, $CDCl_3$) of **10α** δ 5.20 (t, J = 7.5, HC(3′)), 5.05 (dd, J = 7.5, 5.0, HC(2′)), 4.92 (t, J = 7.5, HC(4′)), 4.89 (d, J = 1.5, HC(1)), 4.64 (d, J = 6, HC(6)), 4.40 (d, J = 6, HC(5)), 4.35 (d, J = 5, HC(4)), 4.30 (m, HC(1′)), 4.30 (dd, J = 12.2, 6.8), 4.27 (dd, J = 12.2, 3.0, $H_2C(6')$), 3.90 (ddd, J = 7.5, 6.8, 3.0, HC(5′)), 2.55–2.60 (m, J = 7.0, 5.0, HC(3)), 2.10 (4, s, 4 Ac), 2.08, 1.72 (2 m, $CH_2C(3)$), 1.50, 1.32 (2 s, 2 Me); ^{1}H NMR (360 MHz, $CDCl_3$) of **10β** δ 5.24 (t, J = 9.8, HC(3′)), 5.10 (m, HC(2′)), 4.92 (m, HC(4′)), 4.87 (d, J = 1.5, HC(1)), 4.82, 4.72 (2, d, J = 6.0, HC(5), HC(6)), 4.35 (m, J ≅ 5, 1.5, HC(4)), 4.30, 4.12 (2 m, $H_2C(6')$), 3.68 (m, HC(5′)), 3.18 (m, HC(1′)), 2.80 (m, HC(3)), 2.10 (4 s, 4 Ac), 2.08, 1.65 (2, m, $H_2CC(3)$), 1.48, 1.32 (2 s, 2 Me).

Mixture of (1*S*,4*R*,5*R*,7*R*)-4-*endo*-[(2′,3′,4′,6′-Tetra-*O*-acetyl-α- and -β-D-*gluco*-pyranosyl)methyl]-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-3-one (11α + 11β). Method A. A mixture of **10α/10β** 5.5:1 (100 mg, 0.19 mmol), *m*-chloroperbenzoic acid (mCPBA, Fluka, 80%, 32.7 mg, 0.19 mmol), and $NaHCO_3$ (32 mg, 0.38 mmol) in $CHCl_3$ (5 mL) was stirred at 20 °C for 15 h. After the addition of KF (10 mg), the solvent was evaporated and the residue purified by column chromatography on silica gel (light petroleum/AcOEt (3:1)), yielding 87 mg (96.5%), colorless crystals, of a 5.1:1 mixture of **11α/11β**: mp 77–79 °C. Attempts to recrystallize this mixture from hexane/AcOEt mixture did not lead to enrichment of **11α** or **11β** nor did they lead to a different mp. The existence of **11β** (minor) was deduced from the extra signals seen in the ^{1}H NMR spectrum of **11α**, especially for H-C(1) at δ_H 5.69 ppm: ^{1}H NMR (250 MHz, $CDCl_3$) of **11α** δ 5.70 (s, HC(1)), 5.20 (t, J = 7.5, HC(3′)), 5.08 (dd, J = 7.5, 5.0, HC(2′)), 4.92 (t, J = 7.5, HC(4′)), 4.80 (d, J = 6.0, HC(7)), 4.72 (d, J = 6.0, HC(6)), 4.62 (dd, J = 5.0, HC(5)), 4.48 (m, HC(1′)), 4.30 (dd, J = 12.2, 6.8), 4.18 (dd, J = 12.2, 3.0, $H_2C(6')$), 3.90 (ddd, J = 7.5, 6.8, 3.0, HC(5′)), 3.15 (td, J = 7.0, 5.0, HC(4)), 2.05 (4 s, 4 Ac), 1.80 (m, $CH_2C(4)$), 1.48, 1.32 (2 s, 2 Me); $[\alpha]^{25}_{589}$ = +22°, $[\alpha]^{25}_{578}$ = +23°, $[\alpha]^{25}_{546}$ = +25°, $[\alpha]^{25}_{436}$ = +40°, $[\alpha]^{25}_{365}$ = +56° (c = 15 g/dm^3, CH_2Cl_2). **Method B.** A mixture of racemic **13** (90 mg, 0.42 mmol), α-acetobromoglucose (**7**, 227 mg, 0.55 mmol), and AIBN (5 mg) in anhydrous toluene was heated under reflux and Ar atmosphere. After 5 min of boiling, a solution of Bu_3SnH (206 mg, 0.70 mmol) and AIBN (7 mg) in anhydrous toluene was added slowly through a syringe (ca. 60 min). The solvent was evaporated and the residue purified by column chromatography as in method A. The first fraction gave the reduced glucose derivatives **8** and **9** (75 mg). The second fraction yielded 168 mg (73%) of a 5.5:5.5:1:1 mixture of **11α/11′α/11β/11′β**, **11′α** and **11′β** being the α-*C*- and β-*C*-glucosides whose bicyclic lactone moieties are enantiomeric to those in **11α** and **11β**. The intensity of the signals at δ = 5.70–6.65 ppm (for HC(1)) gave the ratio of **11α/11′α/11β/11′β**.

(1*RS*,4*RS*,5*SR*,6*SR*,7*SR*)-4-*exo*-[(Benzyloxy)methyl]-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-15). A 1.6 M solution of BuLi in hexane (2.4 mL, 1 equiv) was added to a stirred solution of diisopropylamine (640 μL, 1.2 equiv) in anhydrous THF (30 mL) cooled to 0 °C. After being stirred at 0 °C for 15 min, the mixture was cooled to −60 °C, and a solution of (±)-**14** (750 mg, 3.75 mmol)[29] in anhydrous THF (15 mL) cooled to −40 °C was added slowly. After the mixture was stirred at −60 °C for 30 min, (bromomethoxymethyl)benzene (2.5 mL, 8.4 equiv) was added portionwise and the solution was allowed to reach 0 °C in about 20 min. The mixture was poured into a saturated aqueous solution of NH_4Cl cooled to 0 °C. The mixture was extracted with CH_2Cl_2 (50 mL, three times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was immediately purified by column chromatography on silica gel (Lobar, column C, Lichroprep Si 60, 40–63 μm, CH_2Cl_2/Et_2O/light petroleum (3:1:2)), yielding 885 mg (74%), white solid, recrystallized from AcOEt/light petroleum: mp 97–97.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.28–7.42 (m, C_6H_5), 5.70 (d, J = 1.0, HC(1)), 4.83, 4.66 (2 d, J = 5.5, HC(6), HC(7)), 4.78 (d, J = 1.0, HC(5)), 4.59, 4.55 (2 d, J = 11.5, Bn), 3.81 (d, J = 7.2, $CH_2C(4)$), 2.79 (t, J = 7.2, HC(4)), 1.50, 1.34 (2 s, 2 Me).[45]

(44) Gasparini, F.; Vogel, P. *J. Org. Chem.* **1990**, *55*, 2451.

(1*RS*,4*RS*,5*SR*,6*SR*,7*SR*)-4-*exo*-(Hydroxymethyl)-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-16). A mixture of (±)-15 (5.19 g, 18.4 mmol), THF (120 mL), H_2O (25 mL), and 10% Pd on charcoal (8.85 g, 0.45 equiv) was degassed and pressurized with H_2 (1 atm). After shaking for 36 h, the precipitate was filtered off and the solvent evaporated, yielding 4.06 g (96%), colorless crystals, recrystallized from AcOEt/light petroleum (1:3): mp 122.5–123.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.72 (d, J = 1.0, HC(1)), 4.83, 4.71 (2 d, J = 5.5, HC(6), HC(7)), 4.66 (d, J = 1.0, HC(5)), 4.02 (dd, J = 10.5, 6.0), 3.92 (dd, J = 10.5, 7.8, $CH_2C(4)$), 2.68 (dd, J = 7.8, 6.0, HC(4)), 2.60 (s, OH), 1.48, 1.33 (2 s, 2 Me).[45]

[(1*RS*,4*RS*,5*SR*,6*SR*,7*SR*)-6-*exo*,7-*exo*-(Isopropylidenedioxy)-3-oxo-2,8-dioxabicyclo[3.2.1]oct-4-*exo*-yl]methyl Methanesulfonate ((±)-17). A solution of (±)-16 (0.5 g, 2.17 mmol) and CH_3SO_2Cl (0.17 mL, 2.17 mmol) in anhydrous pyridine (10 mL) was stirred at 0 °C for 1 h. The mixture was poured into a saturated aqueous solution of NH_4Cl (50 mL) and extracted with CH_2Cl_2 (50 mL, three times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was recrystallized from MeOH, yielding 650 mg (98%), colorless crystals: mp 83–85 °C.

(1*RS*,5*SR*,6*SR*,7*SR*)-6-*exo*,7-*exo*-(Isopropylidenedioxy)-4-methylidene-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-13). A mixture of CH_3SO_2Cl (240 μL, 3.04 mmol) and (±)-16 (0.5 g, 2.17 mmol) in anhydrous pyridine (10 mL) was stirred at 0 °C for 24 h. The temperature was allowed to reach 25 °C. The solvent was evaporated in vacuum (0.01 Torr) and the residue dissolved in CH_2Cl_2 (50 mL). The solution was washed with a saturated aqueous solution of NH_4Cl (50 mL, twice). The combined aqueous phases were extracted with CH_2Cl_2 (50 mL, twice). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was recrystallized from MeOH, yielding 438 mg (95%), colorless crystals: mp 72–74 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.50 (d, J = 1.0, 1 H, H_2C=C(4)), 5.78 (d, J = 1.0, HC(1)), 5.75 (d, J = 1.0, 1 H, H_2C=C(4)), 5.05 (br s, HC(5)), 4.85, 4.65 (2 d, J = 5.0, HC(6), HC(7)), 1.50, 1.34 (2 s, 2 Me).

Mixture of (+)-Methyl [1-*O*-Acetyl-5-deoxy-2,3-*O*-isopropylidene-5-[(2′,3′,4′,6′-tetra-*O*-acetyl-α- and -β-D-glucopyranosyl)methyl]-α- and -β-L-*talo*-hexofuranosyl]uronate ((+)-19). A 5.5:1 mixture of 11α and 11β ((+)-11, 0.2 g, 0.40 mmol), $NaHCO_3$ (10.5 mg, 0.14 mmol), and anhydrous MeOH (5 mL) was stirred at 20 °C for 15 h. The solvent was evaporated and the residue dissolved in anhydrous pyridine (1 mL). Ac_2O (0.5 mL) and a trace of (dimethylamino)pyridine (DMAP) were added and the mixture stirred at 20 °C for 12 h. The solvent was evaporated in vacuum (0.05 Torr) and the residue filtered through silica gel (AcOEt), yielding 243 mg (97%), colorless oil: $[\alpha]^{25}_{589}$ = +18°, $[\alpha]^{25}_{578}$ = +19°, $[\alpha]^{25}_{546}$ = +22°, $[\alpha]^{25}_{436}$ = +36°, $[\alpha]^{25}_{365}$ = +54° (c = 24 g/dm^3, CH_2Cl_2). Characteristics of methyl [1-*O*-acetyl-5-deoxy-2,3-*O*-isopropylidene-5-[2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-β-L-*talo*-hexofuranosyl]uronate: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.20 (s, HC(1)), 5.22 (t, J = 7.0, HC(3′)), 5.10 (m, J = 7, HC(2′)), 4.90 (m, HC(4′)), 4.72 (d, J = 6.0, HC(3)), 4.70 (m, HC(4)), 4.40 (d, J = 6.0, HC(2)), 4.28 (dd, J = 12.2, 7.0), 4.20 (dd, J = 12.2, 5.0, H_2C(6′)), 3.85 (m, HC(5′)), 3.76 (s, CH_3OOC), 2.75 (td, J = 10, 3.0, HC(5)), 2.3–2.1 and 1.9–1.7 (2 m, H_2C-C(5)), 2.10–2.00 (5 s, 5 Ac), 1.50, 1.35 (2 s, 2 Me). Characteristics of methyl [1-*O*-acetyl-5-deoxy-2,3-*O*-isopropylidene-5-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-α-L-*talo*-hexofuranosyl]uronate: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.17 (d, J = 4.0, HC(1)), 5.22 (t, J = 7.5, HC(3′)), 5.10 (m, J = 7.5, HC(2′)), 4.90 (m, J = 7.5, HC(4′)), 4.72 (d, J = 6.0, HC(3)), 4.70 (m, HC(4)), 4.60 (dd, J = 6.0, 4.0, HC(2)), 4.40 (dd, J = 12.0, 7.0), 4.05 (m, J = 12.0, 4.0, H_2C(6′)), 3.85 (m, HC(5′)), 3.68 (s, CH_3OOC), 2.55 (td, J = 10.0, 3.0, HC(5)), 2.30–2.10, 1.90–1.70 (2, m, H_2CC(5)), 2.10–2.00 (5 s, 5 Ac), 1.50, 1.35 (2 s, 2 Me). These two anomers are present in a 1:1 proportion and represent more then 83% of the mixture.

(+)-2-Deoxy-2-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-3,4,6-tri-*O*-acetyl-L-*altro*-hexono-1,4-lactone ((+)-21) and -1,5-lactone ((+)-22). A mixture of anhydrous K_2CO_3 (40 mg, 0.29 mmol), (+)-19 (100 mg, 0.18 mmol), and anhydrous MeOH (5 mL) was stirred at 20 °C for 1 h. After the mixture was cooled to 0 °C, $NaBH_4$ (80 mg, 2.1 mmol) was added portionwise and the temperature was allowed to reach 20 °C. After being stirred at 20 °C for 4 h, the solvent was evaporated and the residue taken with ice-cold 1 N HCl (5 mL, until pH = 2). The mixture was stirred at 40 °C for 15 h. The solvent was evaporated in vacuo and the residue taken with toluene and evaporated again at 60 °C. The residue was taken in pyridine (2 mL), and then Ac_2O (1 mL) and a trace of DMAP were added. After staying at 20 °C for 7 h, the solvent was evaporated under high vacuum (0.01 Torr) and the residue purified by column chromatography on silica gel (Lobar, Column type A, AcOEt/light petroleum (5:2)). A first fraction afforded 35 mg (31%) of (+)-22; a second fraction yielded 40 mg (36%) of (+)-21, both colorless oils. Characteristics of (+)-21: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.40 (t, J = 5.0, HC(3)), 5.33 (m, J = 5.0, HC(4)), 5.32 (t, J = 9.0, HC(3′)), 5.18 (dd, J = 9.0, 6.0, HC(2′)), 5.05 (t, J = 9.0, HC(4′)), 4.58 (m, HC(1′)), 4.55 (t, J = 5.0, 1 H, HC(5)), 4.40 (dd, J = 12.2, 5.0, 2 H, H_2C(6)), 4.20–4.05 (m, 2 H, H_2C(6′)), 3.95 (m, HC(5′)), 2.35 (m, HC(2)), 2.40, 2.20 (m, H_2C(2)), 2.10–2.00 (7 s, 7 Ac); $[\alpha]^{25}_{589}$ = +23°, $[\alpha]^{25}_{578}$ = +24°, $[\alpha]^{25}_{546}$ = +28°, $[\alpha]^{25}_{436}$ = +50°, $[\alpha]^{25}_{365}$ = +86° (c = 5.2 g/dm^3, CH_2Cl_2). Characteristics of (+)-22: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.48 (dd, J = 6.0, HC(3)), 5.32 (t, J = 9.0, HC(3′)), 5.18 (m, HC(2′)), 5.05 (t, J = 9.0, HC(4′)), 4.52 (d, J = 6.0, HC(4)), 4.48 (dd, J = 12.5, 4.0) & 4.35 (dd, J = 12.5, 4.5, H_2C(6)), 4.20 (dd, J = 12.5, 5.0), 4.05 (dd, J = 12.5, 2.5, H_2C(6′)), 4.20 (m, HC(1)), 3.92 (m, HC(5′)), 3.70 (m, HC(5)), 3.20 (m, HC(2)), 2.35 (2 m, 1 H of H_2CC(2)), 2.15–2.00 (7 s, 7 Ac), 1.75 (m, 1 H of H_2CC(2)); $[\alpha]^{25}_{589}$ = +31°, $[\alpha]^{25}_{578}$ = +31.5°, $[\alpha]^{25}_{546}$ = +36°, $[\alpha]^{25}_{436}$ = +64°, $[\alpha]^{25}_{365}$ = +117° (c = 5.0 g/dm^3, CH_2Cl_2).

(−)-(1*S*,4*R*,5*R*,6*R*)-5-*exo*-(Benzeneselenyl)-6-*endo*-chloro-3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one ((−)-26). A mixture of (−)-25[40b] (2.86 g, 6.87 mmol), *N*,*N*-dimethylmethyleneimmonium iodide (1.865 g, 10.3 mmol), and HMPA (1.23 g, 6.87 mmol) in anhydrous THF was heated under reflux for 24 h. After being cooled to 20 °C, the mixture was poured into CH_2Cl_2 (100 mL) and H_2O (100 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL, 3 times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (Lobar, Column type C, AcOEt/light petroleum (1:3)), yielding 1.834 g (84.2%), colorless oil: UV (CH_3CN) λ_{max} 203 nm (ε = 16 500), 217 (15 000), 265 (2500), 298 (1200); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.62–7.35 (m, C_6H_5), 6.01 (d, J = 1.0) and 5.48 (m, J = 1.0, 0.7, H_2C=C(3)), 5.09 (m, J = 1.0, 1.0, 1.0, 0.7, HC(4)), 4.60 (dd, J = 6.0, 1.0, HC(1)), 4.35 (m, J = 6.0, 3.0, 1.0, HC(6)), 3.60 (d, J = 3.0, HC(5)); $[\alpha]^{25}_{589}$ = −49°, $[\alpha]^{25}_{578}$ = −51°, $[\alpha]^{25}_{546}$ = −55°, $[\alpha]^{25}_{436}$ = −4.5°, $[\alpha]^{25}_{365}$ = +7.7° (c = 18 g/dm^3, CH_2Cl_2).

Mixture of (+)-(1*S*,3*R*,4*R*,5*R*,6*R*)-5-*exo*-(Benzeneselenyl)-6-*endo*-chloro-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α- and -β-D-glucopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-27 and (+)-28). A mixture of (−)-26 (1 g, 3.15 mmol), tetra-*O*-acetylbromo-D-glucose (7, 1.68 g, 4.09 mmol) and AIBN (50 mg) in anhydrous benzene was heated under reflux for 20 min. A solution of Bu_3SnH (0.84 mL, 3.15 mmol) and AIBN (50 mg) in anhydrous benzene (10 mL) was added with a syringe in about 30 min. After boiling for another 60 min, the solvent was evaporated and the residue dissolved in AcOEt (10 mL). The solution was filtered on silica gel (AcOEt) and then purified by column chromatography on silica gel (Lobar, Column C, AcOEt/light petroleum (1:2)). A first fraction gave 7 (0.3 g), a second fraction furnished the reduced D-glucose derivatives 8 + 9 (235 mg), a third fraction yielded 123 mg (6%) of (+)-28, and a fourth fraction afforded 987 mg (48%) of (+)-27. Characteristics of (+)-27: colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.65–7.35 (m, C_6H_5), 5.15 (t, J = 7.0, HC(3′)), 5.00 (dd, J = 7.0, 4.0, HC(2′)), 4.92 (m, J = 6.0, 1.0, HC(4)), 4.90 (t, J = 7.0, HC(4′)), 4.50 (d, J = 5.5, HC(1)), 4.32 (ddd, J = 5.5, 3.0, 1.0, H-C(6)), 4.30 (m, J = 6.0, 4.0, HC(1′)), 4.28 (dd, J = 12.2, 7.0) and 4.10 (dd, J = 12.2, 5.0, H_2C(6′)), 3.72 (m, J = 7.0, 4.0, HC(5′)), 3.62 (d, J = 3.0, HC(5)), 2.75 (m, J = 6.0, HC(3)), 2.12–2.02 (4 s, 4 Ac), 1.98–1.85 (m, J = 15.0, 6.0) and 1.70 (m, J = 15.0, H_2CC(3)); $[\alpha]^{25}_{589}$ = +24°, $[\alpha]^{25}_{578}$ = +26°, $[\alpha]^{25}_{546}$ = +30°, $[\alpha]^{25}_{436}$ = +51°, $[\alpha]^{25}_{365}$ = +82° (c = 21 g/dm^3, CH_2Cl_2). Characteristics of (+)-28: colorless oil;

(45) This compound was prepared first by Mr. J. Wagner in our laboratory, see: Wagner, J. Dissertation, Ecole Polytechnique fédérale de Lausanne, 1991.

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.65–7.35 (m, C_6H_5), 5.02 (t, J = 7, HC(3′)), 5.0 (m, J = 7, HC(2′)), 4.90 (m, HC(4)), 4.85 (m, HC(4′)), 4.48 (d, J = 5, HC(1)), 4.28 (dd, J = 5, 2.5, HC(6)), 4.18 (m, HC(6′a)), 3.95 (dd, J = 12.2, 5.0, HC(6′b)), 3.60 (d, J = 3, HC(5)), 3.42 (m, HC(5′)), 3.10 (m, J = 9.0, 5.0, 2.5, HC(1′)), 2.90 (m, HC(3)), 2.10–2.00 (4s, 4 Ac), 2.0–1.62 (m, $H_2CC(3)$); $[\alpha]^{25}_{589}$ = +47.7°, $[\alpha]^{25}_{578}$ = +49.3°, $[\alpha]^{25}_{546}$ = +56°, $[\alpha]^{25}_{436}$ = +93.2°, $[\alpha]^{25}_{365}$ = +142° (c = 14.7 g/dm^3, CH_2Cl_2).

(+)-(1*R*,2*R*,3*S*,4*R*,5*R*,6*R*)-5-*exo*-(Benzeneselenyl)-6-*endo*-chloro-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol ((+)-29). $NaBH_4$ (150 mg, 3.96 mmol) was added portionwise to a stirred solution of (+)-**27** (900 mg, 1.393 mmol) in 1:1 THF/MeOH (40 mL) cooled to 0 °C. After the solution was stirred at 0 °C for 10 min, 1 N HCl was added (a few drops, pH ≃ 7) and the solution was diluted with CH_2Cl_2 (50 mL) and washed with H_2O (50 mL) and then with brine (50 mL). The combined aqueous layers were extracted with CH_2Cl_2 (50 mL, twice). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated, yielding 900 mg (99.7%), colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.60, 7.30 (2 m, C_6H_5), 5.18 (t, J = 8.0, HC(3′)), 4.95 (dd, J = 8.0, 5.0, HC(2′)), 4.90 (t, J = 8.0, HC(4′)), 4.50 (d, J = 5.5, HC(1)), 4.40 (m, HC(2)), 4.38 (m, HC(6)), 4.25 (m, HC(1′)), 4.22 (m, 1 H of $H_2C(6')$), 4.20 (m, HC(4)), 4.05 (dd, J = 12.2, 3.0, 1 H of $H_2C(6')$), 3.70 (m, J = 8.0, 4.0, HC(5′)), 3.60 (d, J = 5.0, HC(5)), 2.75 (m, OH), 2.42 (m, HC(3)), 2.10–1.97 (4 s, 4 Ac), 1.82 (m, J = 15.0, 9.0, 3.0) and 1.52 (m, J = 15.0, 10.0, 6.0, H_2C-C(3)); $[\alpha]^{25}_{589}$ = +19°, $[\alpha]^{25}_{578}$ = +20°, $[\alpha]^{25}_{546}$ = +22°, $[\alpha]^{25}_{436}$ = +33°, $[\alpha]^{25}_{365}$ = +40° (c = 13 g/dm^3, CH_2Cl_2).

(+)-(1*S*,2*R*,3*S*,4*R*)-6-Chloro-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-7-oxabicyclo[2.2.1]-hept-5-en-2-*endo*-ol ((+)-30). A solution of mCPBA (440 mg, Fluka, 80%, 1.226 mmol) in CH_2Cl_2 (20 mL) was added dropwise (in 20 min) to a stirred solution of (+)-**29** (800 mg, 1.235 mmol) in anhydrous CH_2Cl_2 (20 mL) cooled to −78 °C. After being stirred at −78 °C for 135 min, the mixture was poured into CH_2Cl_2 (50 mL) and a saturated aqueous solution of $NaHCO_3$ (50 mL). The organic phase was collected and the aqueous layer extracted with CH_2Cl_2 (50 mL, twice). The combined organic extracts were washed with brine (50 mL, three times, until pH = 7) and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (Lobar, Column type B, AcOEt/light petroleum (1:1)), yielding 586 mg (96.6%), colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.32 (d, J = 2.0, HC(5)), 5.20 (t, J = 8.0, HC(3′)), 4.96 (dd, J = 8.0, J = 5.0, HC(2′)), 4.90 (t, J = 8.0, HC(4′)), 4.85 (m, HC(4)), 4.65 (d, J = 4.5, HC(1)), 4.52 (m, HC(1′)), 4.30 (m, HC(2)), 4.28 (m, J = 12.2, J = 6.0) & 4.05 (dd, J = 12.2, J = 2.5, $H_2C(6')$), 3.85 (m, J = 8.5, 6, 2.5, H-C(5′)), 2.40 (d, J = 5.5, OH), 2.30 (m, HC(3)), 2.09–2.00 (4 s, 4 Ac), 1.55–1.45 (m, H_2C-C(3)); $[\alpha]^{25}_{589}$ = +34°, $[\alpha]^{25}_{578}$ = +35°, $[\alpha]^{25}_{546}$ = +40°, $[\alpha]^{25}_{436}$ = +67°, $[\alpha]^{25}_{365}$ = +203° (c = 13 g/dm^3, CH_2Cl_2).

(+)-(1*S*,2*R*,3*S*,4*R*)-6-Chloro-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-7-oxabicyclo[2.2.1]-hept-5-en-2-*endo*-yl Acetate ((+)-31). A mixture of (+)-**30** (560 mg, 1.14 mmol), pyridine (5 mL), Ac_2O (3 mL), and DMAP (10 mg) was stirred at 20 °C for 15 h. The solvent was evaporated under vacuum (0.01 Torr). The residue was taken with toluene and the solvent evaporated (0.01 Torr, twice). The residue was taken with AcOEt, decolorized with active charcoal, and filtered through silica gel, yielding 590 mg (97%), colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.35 (d, J = 2.0, HC(5)), 5.20 (t, J = 8.0, HC(3′)), 5.19 (m, J = 8, HC(2′)), 5.00–4.90 (m, HC(4′), HC(1), HC(4), HC(1′)), 4.28 (m, HC(2)), 4.20 (m, J = 12.2, 6.0) and 4.08 (dd, J = 12.2, 2.5, $H_2C(6')$), 3.82 (m, J = 8.0, 6.0, 2.5, HC(5′)), 2.45 (m, HC(3)), 2.10–1.95 (5 s, 5 Ac), 1.95–1.35 (m, $H_2CC(3)$; $[\alpha]^{25}_{589}$ = +66°, $[\alpha]^{25}_{578}$ = +68°, $[\alpha]^{25}_{546}$ = +80°, $[\alpha]^{25}_{436}$ = +129°, $[\alpha]^{25}_{365}$ = +183° (c = 9 g/dm^3, CH_2Cl_2).

(+)-(1*S*,3*R*,4*R*,5*S*,6*R*)-6-*endo*-Acetoxy-3-*exo*-hydroxy-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-methyl]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-33). $NaHCO_3$ (240 mg, 3.5 mmol), 2.5% solution of OsO_4 in CCl_4 (2 drops), and H_2O_2 (30% in H_2O, 2.8 mL) were added successively to a stirred solution of (+)-**31** (470 mg, 0.882 mmol) in THF (30 mL) cooled to 0 °C. After the solution was stirred at 0 °C for 3 h, AcOEt (20 mL) was added and the solution was washed with a 10% aqueous solution of $NaHSO_4$ (20 mL, three times) and then with brine (20 mL, twice). The combined aqueous phases were extracted with AcOEt (20 mL, twice). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated, yielding 480 mg (99%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.22 (t, J = 8.5, HC(3′)), 5.12 (dd, J = 8.5, 6.0, HC(2′)), 4.95 (m, HC(4′)), 4.92 (d, J = 8.0, –OH), 4.60 (d, J = 6.0, HC(4)), 4.59 (d, J = 5.5, HC(1)), 4.33 (m, HC(6)), 4.28 (dd, J = 12.2, 6.0, HC(6′a)), 4.22 (m, HC(1′)), 4.08 (dd, J = 12.2, 2, HC(6′b)), 3.90 (s, HC(3)), 3.85 (m, HC(5′)), 2.58 (m, HC(5)), 2.10–1.95 (5 s, 5 Ac), 1.80 and 1.55 (2 m, $H_2CC(5)$). For derivatives (+)-**32**, (+)-**34**, (+)-**36** and (+)-**38**, see the supplementary material.

(+)-(1*S*,3*R*,4*R*,5*S*,6*R*)-6-*endo*,3-*exo*-Diacetoxy-5-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-35). A mixture of (+)-**33** (117 mg, 0.213 mmol), pyridine (2 mL), Ac_2O (1 mL), and DMAP (10 mg) was stirred at 20 °C for 7 h. The solvent was evaporated in vacuo (0.05 Torr) and the residue taken with AcOEt. The solution was filtered through silica gel. Solvent evaporation yielded 118 mg (94%) of colorless crystals: mp 170–171 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.25 (t, J = 8.5, HC(3′)), 5.18 (dd, J = 8.5, 5.0, HC(2′)), 4.96 (s, HC(3)), 4.95 (m, HC(4)), 4.92 (m, HC(4′)), 4.68 (d, J = 6.0, HC(1)), 4.60 (d, J = 6.0, HC(6)), 4.25 (dd, J = 12.2, 6.0, HC(6′a)), 4.20 (m, HC(1′)), 4.05 (dd, J = 12.2, 2.5, H-C(6′b)), 4.00 (m, HC(5′)), 2.62 (m, H-C(5)), 2.12–2.0 (6 s, 6 Ac), 1.90–1.65 (m, $H_2CC(5)$); $[\alpha]^{25}_{589}$ = +113°, $[\alpha]^{25}_{578}$ = +116°, $[\alpha]^{25}_{546}$ = +135°, $[\alpha]^{25}_{436}$ = +254°, $[\alpha]^{25}_{365}$ = +575° (c = 5 g/dm^3, CH_2Cl_2).

(+)-(1*R*,4*R*,5*R*,6*S*,7*R*)-7-*endo*,4-*exo*-Diacetoxy-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-2,8-dioxabicyclo[3.2.1]octan-3-one ((+)-37). A mixture of $NaHCO_3$ (37 mg, 0.43 mmol), mCPBA (80%, 102.3 mg, 0.47 mmol), and (+)-**35** (256 mg, 0.43 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at 20 °C for 20 min. CH_2Cl_2 (20 mL) was added and the solution washed with a 5% aqueous solution of $NaHCO_3$ (20 mL, twice) and then brine (20 mL). After drying ($MgSO_4$), the solvent was evaporated, yielding 246 mg (94%) of colorless crystals that could be recrystallized from AcOEt/light petroleum: mp 165–166 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.10 (d, J = 4.0, HC(1)), 5.70 (s, HC(4)), 5.25 (t, J = 8.0, HC(3′)), 5.12 (dd, J = 8.0, 5.0, HC(2′)), 4.96 (m, HC(7)), 4.95 (s, HC(5)), 4.92 (t, J = 8.0, HC(4′)), 4.50 (d, J = 6.0, HC(2)), 4.32 (dd, J = 12.0, 6.0, HC(6′a)), 4.28 (m, HC(1′)), 4.05 (dd, J = 12.0, 3.0, HC(6′b)), 3.88 (m, HC(5′)), 2.70 (m, HC(6)), 2.20–2.02 (5 s, 5 Ac), 1.79–1.69 (m, $H_2CC(6)$); $[\alpha]^{25}_{589}$ = +99°, $[\alpha]^{25}_{578}$ = +103°, $[\alpha]^{25}_{546}$ = +117°, $[\alpha]^{25}_{436}$ = +199°, $[\alpha]^{25}_{365}$ = +314° (c = 10 g/dm^3, CH_2Cl_2).

(+)-4-Deoxy-4-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-2,3,6-tri-*O*-acetyl-L-mannono-1,5-lactone ((+)-41). A mixture of (+)-**37** (100 mg, 0.165 mmol), anhydrous K_2CO_3 (10 mg), and anhydrous MeOH (5 mL) was stirred at 20 °C for 45 min. $NaBH_4$ (80 mg, 2.1 mmol) was then added portionwise to the stirred solution cooled to 0 °C. After the mixture was stirred at 25 °C for 4 h, the solvent was evaporated (0.05 Torr). The residue (**40**) was taken with 1 N HCl at 0 °C (pH = 2–3). After stirring at 25 °C for 15 h, the solvent was evaporated in vacuo (0.05 Torr) under heating to 60 °C. The residue was washed with toluene (5 mL, 3 times) and then dissolved in pyridine (2 mL), Ac_2O (1 mL) and DMAP (10 mg). After the solution was stirred at 20 °C for 15 h, the solvent was evaporated (0.05 Torr). The residue was purified by column chromatography on silica gel (Lobar, Column type A, AcOEt/light petroleum (2:1)), yielding 65 mg (62%), colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.42 (dd, J = 7.5, J(H-C(2),H-C(4)) = 2.2, HC(2)), 5.30 (t, J = 9.0, HC(3′)), 5.22 (m, HC(3)), 5.10 (dd, J = 9.0, 5.5, HC(2′)), 5.02 (t, J = 9.0, HC(4′)), 4.38 (m, HC(1′)), 4.33 (m, HC(5)), 4.22 (m, $H_2C(6)$, HC(6′a)), 4.02 (dd, J = 12.2, 2.5, HC(6′b)), 3.88 (m, HC(5′)), 2.20 (m, J = 2.2, HC(4)), 2.10–2.00 (7 s, 7 Ac), 2.00–1.65 (m, $H_2CC(4)$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.6, 170.1, 169.9, 169.6, 169.5, 169.4, 169.3 (7 s), 70.2, 70.0, 69.6, 69.2, 68.8, 68.4, 63.6 (8d, ^1J(C,H) = 150 Hz), 62.1 (t, ^1J(C,H) = 150), 61.7 (t, ^1J(C,H) = 150), 35.1 (d, ^1J(C,H) = 125), 29.7 (t, ^1J(C,H) = 125), 20.9–20.1 (7 q, ^1J(C,H) = 125); MS (CI, NH_3) m/z 654 (100), 650 (28, M + 18), 649 (16), 637 (19), 636 (40), 633 (9), 580 (19), 577 (32), 532 (5), 410 (12), 70 (33); $[\alpha]^{25}_{589}$ = +12°, $[\alpha]^{25}_{578}$ = +13°, $[\alpha]^{25}_{546}$ = +14°, $[\alpha]^{25}_{436}$ = +22°, $[\alpha]^{25}_{365}$ = +39° (c = 8 g/dm^3, CH_2Cl_2).

(+)-Methyl [Methyl 2,4-di-*O*-acetyl-3-deoxy-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-β-L-

***manno*-hexopyranosid]uronate ((+)-42) and (+)-Methyl [Methyl 2,5-di-*O*-acetyl-3-deoxy-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-β-L-*manno*-hexofuranosid]uronate ((+)-43).** Freshly distilled $SOCl_2$ (72 μL, 0.99 mmol) was added slowly to a stirred solution of (+)-37 (100 mg, 0.165 mmol) in anhydrous MeOH (2 mL) at 20 °C. After the solution was stirred at 20 °C for 3 h, the solvent was evaporated (0.05 Torr). The residue was taken with toluene (5 mL) and the solvent evaporated (0.05 Torr, twice). The residue was dissolved in pyridine (5 mL), and Ac_2O (2 mL) and DMAP (5 mg) were added. The mixture was allowed to stay at 20 °C for 15 h. The solvent was evaporated to dryness (0.05 Torr) and the residue purified by column chromatography on silica gel (AcOEt/light petroleum (1:4, then 1:2, 1:1, and 2:1)) gave successively 30.3 mg (29%) of (+)-42 and 29.4 mg (28.5%) of (+)-43. Characteristics of (+)-42: colorless crystals; mp 55–56 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.28 (t, J = 8.5, HC(3′)), 5.18 (d, J = 8.0, HC(2′)), 5.11 (d, J = 4.5, HC(2)), 4.94 (t, J = 8.5, HC(4′)), 4.90 (s, HC(1), 4.52 (t, J = 8.0, HC(4)), 4.28 (dd, J = 12.2, 6, HC(6′a)), 4.22–4.18 (m, HC(1′), HC(5)), 4.10 (dd, J = 12.2, 3, HC(6′b)), 3.88 (m, J = 9.0, 6.5, 2.5, HC(5′)), 3.80 (s, $-COOCH_3$), 3.32 (s, $-OCH_3$), 2.92 (m, HC(3)), 2.20–2.05 (6 s, 6 Ac), 1.95–1.55 (m, $H_2CC(3)$); $[\alpha]^{25}_{589}$ = +16°, $[\alpha]^{25}_{578}$ = +16.5°, $[\alpha]^{25}_{546}$ = +18°, $[\alpha]^{25}_{436}$ = +30°, $[\alpha]^{25}_{365}$ = +48° (c = 8 g/dm^3, CH_2Cl_2). Characteristics of (+)-43: colorless crystals; mp 56–57 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.27 (t, J = 9.0, HC(3′)), 5.10 (dd, J = 9.0, 5.0, HC(2′)), 5.07 (m, HC(1)), 5.00 (m, HC(4′)), 4.90 (t, J = 9.0, HC(4)), 4.74 (d, J = 1.5, HC(5)), 4.25 (m, HC(1′)), 4.22 (m, HC(2)), 4.18 (dd, J = 12.2, 6.0, HC(6′a)), 4.14 (dd, J = 12.2, 3.0, HC(6′b)), 3.80 (m, HC(5′)), 3.75 (s, $-COOCH_3$), 3.40 (s, $-OCH_3$), 2.40 (m, HC(3′)), 2.10–2.00 (6 s, 6 Ac), 1.85 and 1.45 (m, $H_2CC(3)$); $[\alpha]^{25}_{589}$ = +30°, $[\alpha]^{25}_{578}$ = +32°, $[\alpha]^{25}_{546}$ = +36°, $[\alpha]^{25}_{436}$ = +59°, $[\alpha]^{25}_{365}$ = +88° (c = 18 g/dm^3, CH_2Cl_2).

(+)-Methyl 3-Deoxy-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-2,4,6-tri-*O*-acetyl-β-L-*manno*-hexopyranoside ((+)-44). $LiAlH_4$ (20 mg, 0.53 mmol) was added portionwise to a stirred solution of (+)-42 (25 mg, 0.04 mmol) in anhydrous THF (2 mL). After being stirred at 20 °C for 150 min, the mixture was cooled to 0 °C and 5% aqueous solution of HCl was added until pH = 3. The solvent was evaporated (0.01 Torr) under heating to 60 °C. The residue was washed with toluene (5 mL, 3 times). The crystalline residue was grounded and mixed with pyridine (2 mL), Ac_2O (1 mL), and DMAP (5 mg). After the solution was stirred at 20 °C for 15 h, the solvent was evaporated (0.01 Torr) and the residue purified by column chromatography on silica gel (Lobar, Column type A, AcOEt/light petroleum (4:1)), yielding 25 mg (97.5%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$), δ 5.25 (t, J = 9.0, HC(3′)), 5.05–4.98 (m, HC(2′), HC(4), HC(2)), 4.90 (t, J = 9.0, HC(4′)), 4.68 (d, J = 1.5, HC(1)), 4.28–4.05 (m, HC(1′), $H_2C(6)$, $H_2C(6′)$), 3.90–3.78 (m, HC(5), HC(5′)), 3.40 (s, $-OCH_3$), 2.38 (m, HC(3)), 2.15–2.00 (7 s, 7 Ac), 1.75, 1.45 (m, $H_2CC(3)$); $[\alpha]^{25}_{589}$ = +17.5°, $[\alpha]^{25}_{578}$ = +18°, $[\alpha]^{25}_{546}$ = +21°, $[\alpha]^{25}_{436}$ = +35°, $[\alpha]^{25}_{365}$ = +50° (c = 12 g/dm^3, CH_2Cl_2).

(+)-Methyl 3-Deoxy-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)methyl]-2,5,6-tri-*O*-acetyl-β-L-*manno*-hexofuranoside ((+)-45). Same procedure as described for (+)-44, starting with (+)-43: yield 92.5% of colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.32 (t, J = 9, HC(3′)), 5.12–5.00 (m, HC(2), HC(2′), HC(1), HC(4)), 4.98 (t, J = 9, HC(4′)), 4.52 (m, HC(5), HC(6a)), 4.42 (dd, J = 14, 2.5, HC(6b)), 4.28–4.10 (m, HC(1′), HC(6′a)), 4.05 (dd, J = 12.2, 3, HC(6′b)), 3.90 (m, HC(5′)), 3.5 (s, $-OCH_3$), 2.48 (m, HC(3)), 2.15–2.00 (7 s, 7 Ac), 1.85–1.50 (m, $H_2CC(3)$); $[\alpha]^{25}_{589}$ = +32°, $[\alpha]^{25}_{578}$ = +34°, $[\alpha]^{25}_{546}$ = +40°, $[\alpha]^{25}_{436}$ = +63°, $[\alpha]^{25}_{365}$ = +94° (c = 18 g/dm^3, CH_2Cl_2).

(±)-6-Chloro-3-methylidene-7-oxabicyclo[2.2.1]hept-5-en-2-one (46). A solution of mCPBA (80%, 310 mg, 0.88 mmol) in CH_2Cl_2 (10 mL) was added slowly to a stirred solution of (±)-26 (279 mg 0.88 mmol) in anhydrous CH_2Cl_2 (10 mL) cooled to −78 °C. After the solution was stirred at −78 °C for 75 min, KF (10 mg) was added and the mixture was neutralized by addition of a 5% aqueous solution of Na_2CO_3. The mixture was extracted with CH_2Cl_2 (100 mL, twice). The combined extracts were washed with H_2O (100 mL) and then with brine (100 mL). The solvent was evaporated and the residue taken in light petroleum. The precipitate (KF–mCPBA complex) was filtered off and the solution was purified by column chromatography on silica gel (Lobar, Column type B, light petroleum), yielding successively 83 mg (60%) of 46 and 27 mg (10%) of an adduct of PhSeOH to 46. Characteristics of 46: colorless oil; IR ($CHCl_3$) ν 1760, 1670, 1580, 1405, 1240, 1050, 1000, 940 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.57 (d, J = 2.0, HC(5)), 5.88 (d, J = 1.0, 1 H of CH_2=C(3)), 5.49 (m, HC(4)), 5.37 (d, J = 1.0, 1 H of CH_2=C(3)), 4.54 (s, HC(1)); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 205.0, 136.1, (2 s), 134.3 (d, ^1J(C,H) = 180), 129.6 (s), 112.9 (t, ^1J(C,H) = 160), 85.1 (d, ^1J(C,H) = 180), 82.2 (d, ^1J(C,H) = 180); MS (CI,NH_3) m/z 175 (1, M + 18), 158 (25), 157 (28, M$^{\bullet+}$), 78 (100).

Acknowledgment. We are grateful to the Swiss National Science Foundation, the Fonds Herbette (Lausanne), Hoffmann-La Roche and Co., AG (Basel) and E. I. Du Pont de Nemours and Co. (Wilmington, DE) for financial support. We thank also Mr. Francisco Sepulveda and Martial Rey for their technical assistance.

Supplementary Material Available: IR, ^{13}C NMR, and MS spectral data, as well as elemental analysis of new compounds (+)-3, (±)-4, 10α/10β, 11α/11β, 13, 15–17, (+)-19, (+)-21, (+)-22, (−)-26, (+)-38, (+)-42, and (+)-45 and ^{1}H NMR spectra of (+)-41, (+)-44, (+)-45, and 46 (16 pages). This material is contained in many 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.