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Stereoselective Synthesis of 2-Deoxyglycosides from Sulfanyl Alkenes by Consecutive "One Pot" Cyclization and Glycosylation Reactions

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2-Deoxy-2-iodopyranosides **3**, and **9**–**12** were synthesized from sulfanyl alkenes using a "one pot" consecutive cyclization–glycosylation process. Compared with the stepwise procedure, the "one pot" process gave significantly improved yields with similar or slightly lower selectivities. The "one pot" procedure was applied to the synthesis of 2,6-dideoxy-2-iodoglycoside **22**, which was successfully deiodinated to afford the 2,6-dideoxyglycoside **23**.

Introduction

Glycoside domains are present in many natural secondary metabolites with interesting biological properties, including antibiotic, antiparasital and anticancer agents. In addition, glycoconjugates such as lipopolysaccharides, glycoproteins and glycolipids play important roles in numerous biological processes where they act as ligands for cell–cell interactions or as targets for toxins, antibodies and microorganisms[1] (Figure 1). However, glycoconjugates have proved to be difficult to synthesize, which has slowed down efforts to understand their various biological functions. Currently, solution-phase synthesis is the standard approach for elaborate glycoconjugate assembly, and methods such as "one pot" strategies have been developed.[2]

The stereocontrolled construction of deoxyoligosaccharide scaffolds is a complex process for a number of reasons: a) the absence of a substituent at C2 makes it difficult to control the stereoselectivity of the reaction; b) the 2-deoxyglycosyl donors and the product glycosides exhibit increased lability, and need to be handled with particular care; and c) the deoxyglycosidic linkage is very acid labile. Thus, these issues must be resolved when developing a method for constructing such molecules.

We have recently reported a general procedure for the stereoselective synthesis of 2-deoxy-2-iodohexopyranosyl thioglycosides from furanoses, which provides a new method for accessing 2-deoxyoligosaccharides (Scheme 1).[3–5] The procedure involves three reactions: Wittig–Horner olefination to give an alkenyl sulfanyl derivative; electrophilic iodine-induced cyclization to give phenyl 2-deoxy-2-iodo-1-thiopyranosides,[6] a new type of glycosyl donor; and finally glycosylation. The most important aspect of this procedure is that it provides access to 2-deoxy-2-iodoglycosyl donors of *gulo* and *allo* configuration that are not readily accessible, and that the stereochemistry of the [I^+] addition to the alkene is determined by the configuration of the allylic alkoxy group at the alkenyl sulfanyl derivative, with the iodine at C-2 taking on a *cis* configuration with respect to the C-3 alkoxy group in the thioglycoside.

This latter aspect is a key point in the overall process because the iodine controls the stereoselectivity of the glycosylation reaction. An additional important aspect is that the glycosylation reaction proceeds with good yields and good to excellent stereoselectivity. The glycosidic bond created in the major isomers is always *trans* to the iodine substituent at C-2.

In the procedure described, the 2-deoxy-2-iodothioglycoside, which is prepared from acyclic derivatives via [I^+]-induced cyclization, is isolated and further activated in the presence of a glycosyl acceptor, an [I^+] equivalent and triflic acid (TfOH) to give the corresponding 2-deoxy-2-iodoglycoside. The similar conditions required for cyclization and glycosylation prompted us to explore the construction of 2-deoxy-2-iodo-oligosaccharide motifs through a more direct strategy that does not require the isolation of the 2-deoxy-2-iodothioglycoside.

Herein we report a convenient consecutive "one pot" electrophile-induced cyclization–glycosylation sequence from the corresponding acyclic alkenyl sulfanyl derivative to directly furnish the 2-deoxy-2-iodoglycoside (Scheme 2). We show that this "one-pot" procedure in general gives better yields than the stepwise procedure, with remarkable improvements in some cases, and with only a slight loss of stereoselectivity in the final glycoside. In addition, we show

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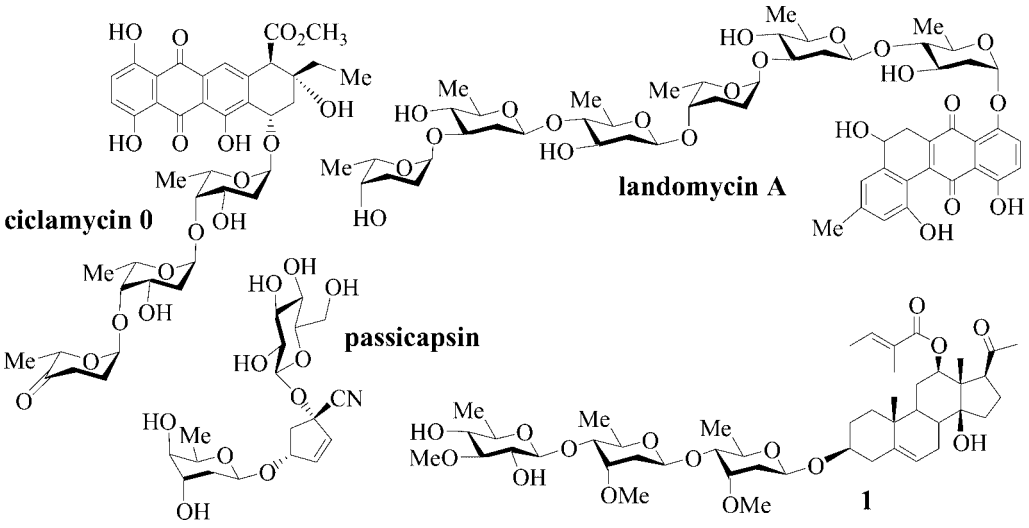
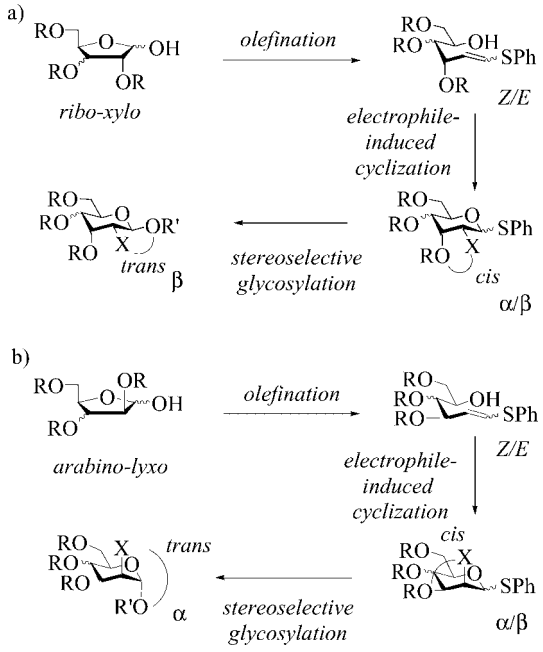
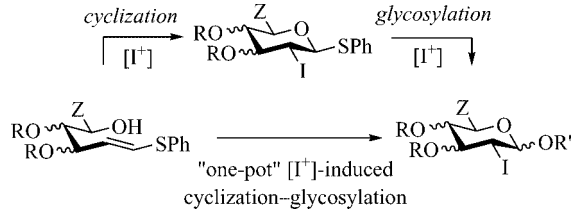


Figure 1. Examples of 2-deoxyoligosaccharide molecules containing configurationally different 2-deoxysugars.



Scheme 1. General Scheme for the synthesis of 2-deoxy-2-iodopyranosylglycosides from pento-furanoses.



Scheme 2. Refinement of the original stepwise sequential procedure in a more efficient "one-pot" cyclization–glycosylation procedure.

that this methodology can be used to prepare a 2,6-dideoxyglycoside related to the pregnane glycoside **1** with appetite-suppressing activity (Figure 1).[7]

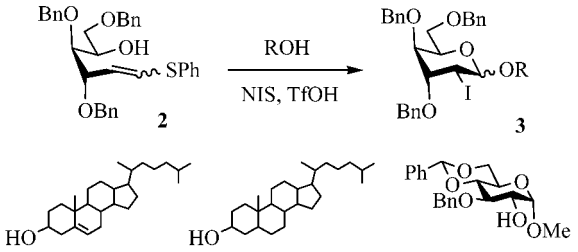
Results and Discussion

To facilitate comparison between the "one pot" and stepwise procedures, consecutive cyclization–glycosylation was initially studied using starting materials and glycosyl acceptors similar to those used previously in the two step procedure. First we considered the *xylo* derivative **2**. In a previous study,[3] reagents such as *N*-iodosuccinimide (NIS) and iodonium dicollidine perchlorate (IDCP) were used to perform [I$^+$]-induced cyclization to give the corresponding 2-deoxy-2-iodothioglycosides. When applied to the consecutive cyclization–glycosylation strategy, IDCP led to the thioglycoside but was ineffective in bringing about glycosylation even with addition of TfOH. Consequently, the following experiments were carried out using NIS, which was found to promote both transformations to directly afford the 2-iodoglycoside.

Table 1 shows representative examples of the different reaction conditions tested. The initial assay from **2** was carried out using 2 equiv. of cholesterol[8] (**4a**) as the glycosyl acceptor and 5 equiv. of NIS. The reaction mixture was stirred for 2 h at low temperature (from –60 °C to –40 °C), and then TfOH was added to promote glycosylation to afford the glycoside **3a** in 33% yield (Table 1, entry 1). In view of the moderate yields obtained, the reaction conditions were optimized. The improved reaction conditions can be summarized as follows: a) Only 3 equiv. of NIS are necessary to promote the desired transformation. b) Monitoring of the progress of the reactions by TLC is crucial for achieving overall good yields, with TfOH only being added when the cyclization is complete. c) To achieve good stereoselectivity for the final glycoside **3a**, glycosylation of cholesterol with the initially formed transient thioglycoside must take place at ca. –50 °C.

This is achieved by addition of TfOH at –50 °C and careful temperature control. The optimized reaction of **2** and **4a** gave glycoside **3a** in 66% yield (i.e., doubled yield compared to the nonoptimized reaction) and with a similar

Table 1. Stereoselective synthesis of glycoside **3** from **2** by consecutive cyclization and glycosylation.[a]



Entry	ROH	NIS/**2** ratio	Product	Yield (%)	α/β ratio[b]
1[c]	**4a**	5:1	**3a**	33	14:86
2[d]	**4a**	3:1	**3a**	66 (51)[e]	12:88 (11:89)[e]
3[d]	**4b**	3:1	**3b**	76	6:94
4[d]	**4c**	3:1	**3c**	71 (47)[e]	9:91 (6:94)[e]

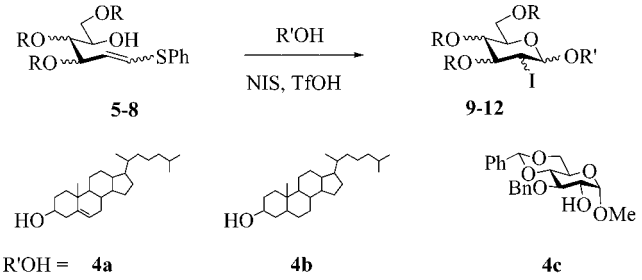
[a] For the *Z*/*E* ratio of the starting alkene, see Exp. Sect. [b] Determined by integration of the anomeric proton signals in the ^{1}H NMR spectrum of the crude reaction mixture. [c] Unoptimized reaction. [d] Optimized conditions: compound **2** (1 mmol) and ROH (2 mmol) were treated with NIS (3 mmol) in CH_2Cl_2 (25 mL) at –60 °C to –10 °C until no alkene was observed. The reaction mixture was then cooled to –60 °C and TfOH (0.2 mmol) was added. The reaction temperature was then allowed to rise to –10 °C and maintained at this temperature until the completion of the reaction. [e] Yield and selectivity values in brackets correspond to the stepwise procedure.

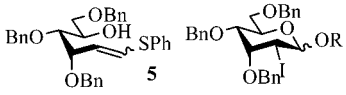
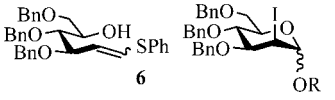
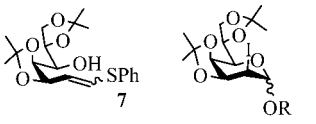
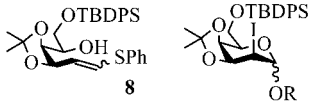
selectivity to that obtained in the stepwise procedure (entry 2). Similar behavior was observed for the reaction of **2** with cholestanol (**4b**) and the glycoside derivative **4c** (entries 3 and 4, respectively).

Especially remarkable is the reaction of **2** with cholestanol, which affords glycoside **3b** in good yield (76%) and with excellent stereoselectivity despite starting from an alkenyl sulfide with a higher percentage of the less reactive *Z* isomer (entry 3).[9] Globally, the "one pot" procedure provides yields around 70%, which is clearly better than those of the stepwise procedure, with only a slight decrease in the stereoselectivity of the final glycoside (entries 2, 4).

We also tested the consecutive reaction using the substrates **5**–**8** with *ribo*, *arabino*, *manno* and *lyxo* configurations, respectively. For the *ribo* derivative **5**, the yields were slightly higher than those of the stepwise procedure, and the stereoselectivity was maintained when alcohol **4c** was used as the glycosyl acceptor, but decreased for cholesterol (Table 2, entry 1). Similarly, for the *arabino* derivative **6**, the overall yields were higher for the "one pot" procedure, and the stereoselectivity for both glycosyl acceptors tested was close to that of the stepwise procedure (entry 2). The results obtained for the sulfanyl alkenes **7** and **8** were even more remarkable: yield increases of 20–38% were observed, with no loss of stereoselectivity when alcohol **4c** was the glycosyl acceptor (entry 3). However, significant decreases in the stereoselectivity were observed when cholestanol and cholesterol were used as the glycosyl acceptors, with cholesterol showing an especially large decrease (entries 3, 4), consistent with previous reports on the behavior of less sterically hindered acceptors.[4b]

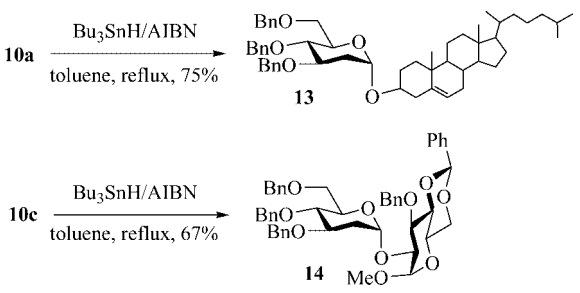
Table 2. Stereoselective consecutive cyclization–glycosylation reactions from sulfanyl alkenes **5**–**8**.[a,b]



Entry	Starting material	Product	Yield (%)[c]	α/β ratio[c,d]
1		**9a** 70 (57) **9c** 65 (62)		25:75 (15:85) 17:83 (10:90)
2		**10a** 54 (43) **10c** 50 (43)		96:4 (97:3) 95:5 (96:4)
3		**11a** 58 (27) **11b** 64 **11c** 71 (33)		66:33 (84:11) 75:25 97:3 (97:3)
4		**12c** 50 (32)		85:15 (95:5)

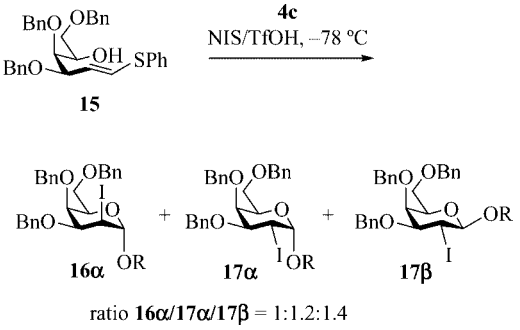
[a] Conditions: Compounds **5**–**8** (1 mmol) and ROH (2 mmol) were treated with NIS (3 mmol) in CH_2Cl_2 (25 mL) at –60 °C to –10 °C until no alkene was observed. The reaction mixture was then cooled to –60 °C and TfOH (0.2 mmol) was added. The reaction temperature was then allowed to rise to –10 °C and maintained at this temperature until the completion of the reaction. [b] For the *Z*/*E* ratio of the starting alkene, see Exp. Sect. [c] Yield and selectivity values in brackets correspond to the stepwise procedure. [d] Determined by integration of the anomeric proton signal in the ^{1}H NMR spectrum of the crude reaction mixture.

2-Deoxyglycosides can easily be obtained from the 2-deoxy-2-iodoglycosides by reaction with Bu_3SnH under radical conditions, as exemplified by conversion of compounds **10a** and **10c** into **13** and **14**, respectively (Scheme 3).[10]



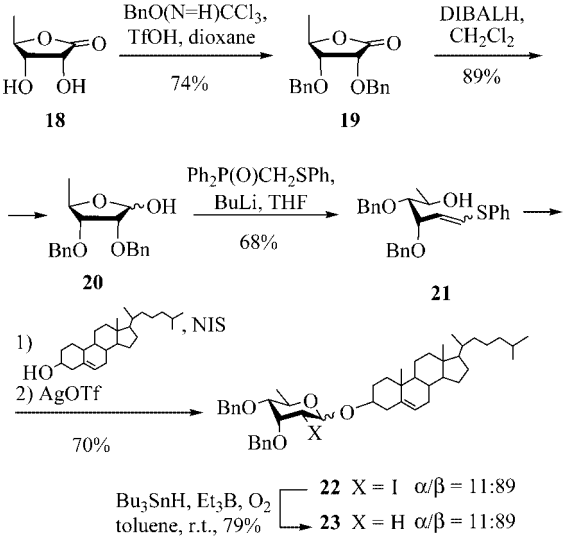
Scheme 3. Deiodination of 2-deoxy-2-iodoglycosides **10a** and **10c**.

Application of the "one pot" cyclization–glycosylation strategy to the *lyxo* derivative **15** led to the formation of a mixture of glycosides **16α** and **17α**,**β**. The overall yield was 82%, significantly higher than that obtained using the stepwise procedure, for which only the cyclization was carried out rendering 35% yield of a mixture of thioglycosides.[3] Compounds **17α**,**β** presumably resulted from an *outside* attack of the electrophile to the alkene, as already was observed in the two step procedure (Scheme 4).



Scheme 4. "One-pot" cyclization–glycosylation procedure of the *lyxo* derivative **15**.

To show the usefulness of the "one pot" cyclization–glycosylation procedure, we applied it to the sulfanyl alkene **21** as a model of the 2,6-dideoxyglycoside constituent of the pregnane glycoside **1**. We also selected cholesterol as a model of the aglycon in **1**. Compound **21** was prepared according to the synthetic route shown in Scheme 5. The lactone **18**[11] was dibenzylated to obtain **19** in 74% yield. Further reduction with di-isobutylaluminium hydride (DIBALH) afforded **20**, which was then treated with $Ph_2P(O)CH_2SPh$ in the presence of *n*-BuLi to afford **21** in 61% overall yield from the protected lactone. The reaction of **21** with cholesterol in the presence of NIS/TfOH afforded **22** in 61% yield (α/β ratio 25:75). Using NIS/AgOTf,[12] the yield increased to 70% and the stereoselectivity



Scheme 5. Application of the "one-pot" cyclization–glycosylation procedure to the synthesis of 2,6-dideoxyglycoside **23**.

improved to an α/β ratio of 11:89. The removal of the iodine atom from **22**, which occupied the equatorial position, proved to be much more difficult than for derivatives **10a**,**c**. When Bu_3SnH/AIBN in refluxing toluene was used, mainly degradation products were obtained. Finally, using Et_3B/O_2[13] at room temperature the 2,6-dideoxyglycoside **23** was obtained in 79% yield.

Conclusions

We have shown that the "one pot" consecutive cyclization–glycosylation strategy is a convenient and direct method for the synthesis of 2-deoxy-2-iodoglycosides that proceeds with good overall yield and stereoselectivity. Compared to classical glycosylation methods, the "one pot" procedure has the advantage that it starts directly from the very stable acyclic alkenyl sulfide precursors and does not require isolation of the glycosyl donors.

The overall strategy (olefination from the pentoses, cyclization–glycosylation reaction) is fairly straightforward and operationally simple. It is worth mentioning that although olefination affords *Z*/*E* mixtures of alkenes, no separation is required because the cyclization is stereospecific at C-2, whose iodine substituent is the stereodirecting group in the glycosylation. This strategy is of particular interest in synthetic routes involving sensitive dideoxyglycosyl donors, and has been successfully applied to the synthesis of the 2,6-dideoxy-2-iodoglycoside **22**, and the corresponding 2,6-dideoxyglycoside **23**.

Experimental Section

General Remarks: Optical rotations were measured at room temperature in 10-cm cells in a Perkin–Elmer 241 polarimeter. ^1H, ^{13}C and ^{31}P NMR spectra were recorded using 300 MHz and 400 MHz spectrometers, with $CDCl_3$ as the solvent and Me_4Si as an internal reference. Elemental analyses were performed using a Carlo–Erba Microanalyzer. Flash column chromatography was performed using silica gel 60 A CC (230–400 mesh). Radial chromatography was performed on 1, 2 or 4 mm plates of Kieselgel 60 PF_{254} silica gel, depending on the amount of product. Solvents were purified using standard procedures.

General "One Pot" Cyclization–Glycosylation Procedure Starting from Sulfanyl Alkenes: The starting alkene (1 mmol), glycosyl acceptor (2 mmol), and molecular sieves (4 Å) (500 mg) in 25 mL (0.02 M) of dry CH_2Cl_2 were stirred together at room temp. for 30 min. The reaction mixture was then cooled to –65 °C and NIS (3.0 mmol) was added. The temperature of the reaction mixture was allowed to increase to –10 °C and then maintained at this temperature and stirred until the cyclization was complete; during this period, the progress of the reaction was monitored by TLC (EtOAc/hexane, 1:3). The reaction mixture was then cooled to –60 °C and TfOH (0.2 mmol) was added. The reaction was stirred at low temperature (between –40 °C and –10 °C) until the reaction was complete. The crude product was extracted with $NaHCO_3$–$Na_2S_2O_3/CH_2Cl_2$. The organic layer was dried with anhydrous $MgSO_4$ and the solvents evaporated. The crude product was purified by chromatographic techniques.

Cholesteryl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-iodo-α/β-D-*gulo*-pyranoside (3a): The title compound (35 mg, 66% yield, α/β = 12:88) was synthesized from **2** (30 mg, 0.057 mmol, *Z*/*E* = 1:5) following the general procedure. The characterization data are coincident to those reported in ref.[3].

3β-Cholestanyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-iodo-α/β-D-*gulo*-pyranoside (3b): The title compound was prepared from **2** (*Z*/*E* ratio 1:2) (100 mg, 0.19 mmol), cholestanol (148 mg, 0.38 mmol), and molecular sieves (4 Å) (100 mg) in 7.8 mL (0.02 M) of dry CH_2Cl_2, following the general procedure. The crude product was purified by radial chromatography (from hexane to EtOAc/hexane 1:4) to afford **3b** (135 mg, 76%) as an inseparable 6:94 α:β mixture as a colourless syrup. R_f(EtOAc/hexane, 1:4) = 0.57. Spectroscopic data extracted from the anomeric mixture are given below.

3bβ: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.17 (m, 15 H), 4.82 (d, $^3J_{H,H}$ = 9.6 Hz, 1 H), 4.66–4.42 (m, $^3J_{H,H}$ = 12.0, 12.4, 13.6 Hz, 6 H), 4.36 (dd, $^3J_{H,H}$ = 9.6, 3.2 Hz, 1 H), 4.16 (dd, $^3J_{H,H}$ = 7.0, 7.0 Hz, 1 H), 3.78 (pseudo t, $^3J_{H,H}$ = 3.2 Hz, 1 H), 3.56 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H), 3.52–3.54 (m, 1 H), 3.34 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H), 1.96–0.54 (m, 45 H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 138.4–137.7 (C_{Ar}), 128.6–127.7 (CH_{Ar}), 98.8, 79.4, 78.9, 74.1, 73.8, 73.5, 72.9, 72.8, 69.2, 33.7 (C-I), 56.7–12.3 (26 C cholestanol) ppm.

3bα: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.18 (m, 15 H), 5.24 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 4.74–4.48 (m, 6 H), 4.17–4.09 (m, 2 H), 3.89–3.83 (m, 2 H), 3.75–3.70 (m, 2 H), 3.53 (m, 1 H), 1.98–0.54 (m, 45 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 138.2–137.7 (C_{Ar}), 128.7–127.7 (CH_{Ar}), 99.4, 81.8, 79.7, 79.2, 75.1, 73.7, 72.8, 71.3, 68.6, 32.8 (C-I), 56.7–12.3 (26 C cholestanol) ppm. $C_{54}H_{75}IO_5$ (931.07): calcd. C 69.66, H 8.12; found C 69.35, H 8.15.

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-iodo-α/β-D-*gulo*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (3c): The title compound (31 mg, 71% yield, α/β = 9:91) was synthesized from **2** (25 mg, 0.047 mmol, *Z*/*E* = 1:5) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Cholesteryl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-iodo-α/β-D-*allo*-pyranoside (9a): The title compound (136 mg, 70% yield, α/β = 25:75) was synthesized from **5** (110 mg, 0.21 mmol, *Z*/*E* = 1:2) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-iodo-α/β-D-*allo*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (9c): The title compound (119 mg, 65% yield, α/β = 17:83) was synthesized from **5** (107 mg, 0.20 mmol, *Z*/*E* = 1:2) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Cholesteryl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-iodo-α/β-D-*manno*-pyranoside (10a): The title compound (143 mg, 54% yield, α/β = 96:4) was synthesized from **6** (150 mg, 0.28 mmol, *Z*/*E* = 2:3) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-iodo-α/β-D-m*anno*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (10c): The title compound (127 mg, 50% yield, α/β = 95:5) was synthesized from **6** (150 mg, 0.28 mmol, *Z*/*E* = 1:3) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Cholesteryl 2-Deoxy-2-iodo-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-α/β-D-*talo*-heptopyranoside (11a): The title compound (145 mg, 58% yield, α/β = 66:33) was synthesized from **7** (120 mg, 0.24 mmol, *Z*/*E* = 0:1) following the general procedure. The characterization data are coincident to those reported in ref.[3]

3β-Cholestanyl 2-Deoxy-2-iodo-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-α/β-D-*talo*-heptopyranoside (11b): Compound **7** (*Z*:*E* = 0:1, 55 mg, 0.150 mmol), cholestanol (116 mg, 0.300 mmol), and molecular sieves (4 Å) (60 mg) in 5.8 mL (0.026 M) of dry CH_2Cl_2 were stirred together at room temp. for 30 min. The reaction was cooled to –65 °C and then NIS (101 mg, 0.45 mmol) was added. The reaction was monitored by TLC (EtOAc/hexane, 1:3) and the reaction temperature was left to rise to –10 °C until the cyclization was complete (4 h). TfOH (2.6 μL, 0.030 mmol) was then added at –60 °C, and the reaction mixture was stirred (–60 °C to –40 °C) for 4 h. The crude product was extracted with $NaHCO_3$–$Na_2S_2O_3$/CH_2Cl_2. The organic phase was dried with anhydrous $MgSO_4$ and the solvents evaporated. The crude product was purified by radial chromatography (from hexane to EtOAc/hexane, 1:4) to afford **11b** (74 mg, 64%) as an inseparable 75:25 α:β mixture in the form of a colourless syrup. R_f(EtOAc/hexane, 1:4) = 0.34. Spectroscopic data extracted from the anomeric mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.19 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 4.64 (dd, $^3J_{H,H}$ = 2.8, 4.0 Hz, 1 H), 4.55 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H), 4.53 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 4.37 (m, 2 H), 4.21 (m, 2 H), 4.07 (m, 4 H), 3.98 (dd, $^3J_{H,H}$ = 7.8, 2.8 Hz 1 H), 3.92 (m, 1 H), 3.77 (dd, $^3J_{H,H}$ = 9.0, 9.2 Hz, 1 H), 3.70 (dd, $^3J_{H,H}$ = 1.6, 7.8 Hz, 1 H), 3.58 (dd, $^3J_{H,H}$ = 1.2, 8.0 Hz, 1 H), 3.53 (m, 1 H), 1.98–0.61 (m, 45 H), 1.52 (s, 3 H), 1.51 (s, 3 H), 1.48 (s, 3 H), 1.42 (s, 3 H), 1.41 (s, 3 H), 1.39 (s, 3 H), 1.38 (s, 3 H), 1.36 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 110.5, 109.7, 109.7, 109.6, 101.2, 100.5, 82.5, 80.1, 77.4, 76.6, 74.2, 74.1, 73.9, 73.6, 73.5, 69.6, 67.3, 66.9, 34.5 (C-2β), 24.2 (C-2α) ppm. 56.7–12.2 (26 C cholestanyl + 4 Me). $C_{40}H_{67}IO_6$ (770.86): calcd. C 62.32, H 8.76; found C 62.22, H 8.79.

Methyl (2′-Deoxy-2′-iodo-3′,4′:6′,7′-di-*O*-isopropylidene-D-*glycero*-α/β-D-*talo*-heptopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (11c): The title compound (132 mg, 71% yield, α/β = 97:3) was synthesized from **7** (90 mg, 0.24 mmol, *Z*/*E* = 1:1.8) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Methyl (6′-*O*-*tert*-Butyldiphenylsilyl-2′-deoxy-2′-iodo-3′,4′-*O*-isopropylidene-α/β-D-*talo*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (12c): The title compound (41 mg, 50% yied, α/β = 85:15) was synthesized from **8** (47.8 mg, 0.089 mmol, *Z*/*E* = 2:5) following the general procedure. The characterization data are coincident to those reported in ref.[3]

Cholesteryl 3,4,6-Tri-*O*-benzyl-2-deoxy-α/β-D-*arabino*-pyranoside (13): To a dry and degassed toluene solution (2 mL) of cholesteryl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α/β-D-*manno*-pyranoside (140 mg, 0.15 mmol) were added AIBN (3.3 mg, 0.0196 mmol) and Bu_3SnH (80 μL, 0.33 mmol). The resulting mixture was heated under reflux for 2.5 h and the toluene evaporated. The crude product was diluted with aqueous saturated KF, extracted with Et_2O, dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification of the crude product by radial chromatography (from hexane to EtOAc/hexane, 1:5) afforded the 2-deoxy product (90.5 mg, 75%) as an inseparable 10:1 α/β anomeric mixture. **13α**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.16 (m, 15 H), 5.28 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H), 5.14 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H), 4.89 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H), 4.71–4.60 (m, 3 H), 4.58–4.46 (m, 2 H), 4.06–3.99 (m, 1 H), 3.87–3.77 (m, 2 H), 3.69–3.60 (m, 2 H), 3.46 (m, 1 H), 2.29–0.67 (m, 45 H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 141.0, 139.0–138.3 (C_{Ar}), 128.6–127.7 (CH_{Ar}), 121.8, 95.2, 78.6, 78.0, 76.0, 75.2, 73.6, 71.9, 70.8, 69.1, 56.9–12.0 (24C cholesterol)

ppm. $C_{54}H_{74}O_5$ (803.16): calcd. C 80.75, H 9.29; found C 80.73, H 9.26.

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-α/β-D-*arabino*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*gluco*-pyranoside (14): To a dry and degassed toluene solution (1.3 mL) of methyl (3′,4′,6′-tri-*O*-benzyl-2′-deoxy-2′-iodo-α/β-D-*manno*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*gluco*-pyranoside (93.6 mg, 0.10 mmol) were added AIBN (2.2 mg, 0.0133 mmol) and Bu_3SnH (67 μL, 0.23 mmol). The resulting mixture was heated under reflux for 2.5 h and the toluene evaporated. The crude product was diluted with aqueous saturated KF, extracted with Et_2O, dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification of the crude product by radial chromatography (from hexane to EtOAc/hexane, 1:3) afforded the 2-deoxy product (54.4 mg, 67%) as an inseparable 20:1 α/β anomeric mixture. **14α**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.02 (m, 25 H), 5.55 (s, 1 H), 5.12 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H), 4.92 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H), 4.91 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H), 4.77 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H), 4.71 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H), 4.67 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H), 4.59 (d, $^3J_{H,H}$ = 12 Hz, 1 H), 4.55 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H), 4.35 (d, $^3J_{H,H}$ = 12 Hz, 1 H), 4.29 (dd, $^3J_{H,H}$ = 10, 4.4 Hz, 1 H), 4.13–4.06 (m, 2 H), 3.94–3.84 (m, 2 H, H-2), 3.81 (m, 1 H), 3.71 (dd, $^3J_{H,H}$ = 10, 20 Hz, 1 H), 3.65–3.61 (m, 1 H), 3.61–3.49 (m, 3 H), 3.44 (s, 3 H), 2.41 (dd, $^3J_{H,H}$ = 13.0, 4.8 Hz, 1 H), 1.80 (t, $^3J_{H,H}$ = 13 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 139.1–137.5 (C_{Ar}), 129.1–126.1 (CH_{Ar}), 101.3, 97.3, 94.1, 82.2, 78.3, 77.6, 77.3, 76.0, 75.0, 73.4, 73.3, 72.1, 70.6, 69.2, 68.6, 62.5, 55.4, 35.5 ppm. $C_{48}H_{52}O_{10}$ (788.92): calcd. C 73.08, H 6.64; found C 72.97, H 6.66.

2,3-Di-*O*-benzyl-5-deoxy-γ-D-ribonolactone (19):[14] A solution of 5-deoxy-γ-D-ribonolactone[10] (**18**) (200 mg, 1.51 mmol) in dry dioxane (10 mL, 0.15 M) was cooled to 0 °C, and then freshly distilled benzyl trichloroacetimidate (790 μL, 4.23 mmol) was added. TfOH was added (20 μL, 0.23 mmol) to ensure that the mixture was strongly acidic and the solution was stirred for 12 h at room temp. (TLC control). The reaction was quenched with saturated aqueous $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (60 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified by radial chromatography (from hexane/AcOEt, 3:1 to hexane/AcOEt, 2:1) to give the title compound (349 mg, 74%) as a white foam. $[\alpha]_D^{20}$ = +26.01 (c = 0.69, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.26 (m, 10 H), 4.94 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H), 4.75 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H), 4.68 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H), 4.63 (dd, $^3J_{H,H}$ = 6.4, 4.0 Hz, 1 H), 4.54 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H), 4.12 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H), 3.75 (dd, $^3J_{H,H}$ = 5.2, 4.0 Hz, 1 H), 1.34 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 172.0, 138.6, 137.2, 128.7, 128.6, 128.4, 128.1, 127.9, 79.1, 78.9, 72.8, 72.4, 18.6 ppm. $C_{19}H_{20}O_4$ (312.36): calcd. C 73.06, H 6.45; found C 73.09, H 6.44.

2,3-Di-*O*-benzyl-5-deoxy-α/β-D-ribofuranose (20). A 1.0 M solution of DIBALH in CH_2Cl_2 (1.58 mL, 1.58 mmol) was added dropwise to a solution of **19** (328 mg, 1.05 mmol) and CH_2Cl_2 (10.5 mL, 0.1 M) at –78 °C. The reaction was monitored by TLC (EtOAc/hexane, 1:3) until the starting product was consumed. After 5 h at –78 °C, the reaction was quenched by adding methanol (3 mL) and warmed to room temp. After adding a mixture of AcOEt/H_2O (1:1) (100 mL), the solution was acidified with diluted sulfuric acid until pH 3 was reached. The aqueous phase was extracted three times with additional AcOEt. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (20 mL), dried (anhydrous $MgSO_4$) and rotaevaporated. The residue was purified by radial chromatography (EtOAc/hexane, 1:3) to afford 294 mg (89%) of **20** as a colourless syrup. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37–7.30 (m, 20 H), 5.35 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H), 5.30 (dd, $^3J_{H,H}$ = 11.2, 4.4 Hz, 1 H), 4.73–4.45 (m, 8 H), 4.33 (qd, $^3J_{H,H}$ = 3.2, 6.4 Hz, 1 H), 4.29 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H), 4.23 (dq, $^3J_{H,H}$ = 6.4, 7.6 Hz, 1 H), 3.93 (dd, $^3J_{H,H}$ = 4.4, 4.8 Hz, 1 H), 3.85 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H), 3.79 (dd, $^3J_{H,H}$ = 7.6, 4.8 Hz, 1 H), 3.62 (dd, $^3J_{H,H}$ = 4.8, 3.2 Hz), 3.30 (br. d, $^3J_{H,H}$ = 3.6 Hz, 1 H), 1.32 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H), 1.17 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 137.9–137.5 (C_{Ar}), 128.7–128.0 (CH_{Ar}), 100.2, 96.0, 82.8, 81.9, 80.5, 77.4, 77.3, 77.2, 73.0, 72.9, 72.6, 72.4, 20.7, 19.9 ppm. $C_{19}H_{22}O_4$ (314.38): calcd. C 72.59, H7.05; found C 72.63, H 7.03.

(*E*/*Z*)-3,4-Di-*O*-benzyl-1,2,6-trideoxy-1-phenylsulfanyl-D-*ribo*-hex-1-enitol (21): To a solution of diphenyl(phenylsulfanylmethyl)phosphane oxide (575 mg, 1.77 mmol) in THF (2.4 mL, 0.74 M) at –78 °C was added 1.6 M *n*-BuLi in hexane (1.2 mL, 1.86 mmol). The mixture was left to stir at low temperature for 30 min. A solution of **20** (150 mg, 0.44 mmol) in THF (2 mL, 0.22 M) was then added dropwise. The mixture was warmed to room temperature overnight (17 h). A saturated solution of NH_4Cl was then added and the olefination product was extracted with dichloromethane. The combination of organic layers was dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash chromatography (EtOAc/hexane, 1:4) to afford the title compound (126 mg, 68%) as an inseparable *E*:*Z* (5:2) diastereoisomeric mixture. Data obtained for the *E*/*Z* mixture. **21*E***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.22 (m, 10 H), 6.50 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H), 5.81 (dd, $^3J_{H,H}$ = 8.4, 15.2 Hz, 1 H), 4.81–4.37 (m, 4 H), 4.03 (dd, $^3J_{H,H}$ = 8.4, 6.8 Hz, 1 H), 3.93 (m, 1 H), 3.36 (dd, $^3J_{H,H}$ = 6.8, 6.0 Hz, 1 H), 2.64 (br. s, 1 H), 1.21 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 138.4–127.2 (C_{Ar}, CH_{Ar}), 129.3, 129.0, 84.5, 81.8, 74.7, 70.6, 69.3, 19.1 ppm. **21*Z***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37–7.21 (m, 10 H), 6.59 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H), 5.92 (pseudo t, $^3J_{H,H}$ = 9.2 Hz, 1 H), 4.81–4.37 (m, 5 H), 3.93 (m, 1 H), 3.49 (dd, $^3J_{H,H}$ = 5.6, 6.4 Hz, 1 H), 2.63 (br. s, 1 H, OH), 1.23 (d, $^3J_{H,H}$ = 6.81 Hz) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 138.4–127.2 (C_{Ar}, CH_{Ar}), 129.4, 129.2, 84.7, 77.6, 74.6, 70.9, 69.1, 19.3 ppm. $C_{26}H_{28}O_3S$ (420.56): calcd. C 74.25, H 6.71, S 7.62; found C 74.20, H 6.69, S 7.60.

Cholesteryl 3,4-Di-*O*-benzyl-2,6-dideoxy-2-iodo-α/β-D-*allo*-pyranoside (22): Compound **21** (*E*:*Z* = 5:2, 48 mg, 0.11 mmol), cholesterol (55 mg, 0.13 mmol), and molecular sieves (4 Å) (40 mg) in 3 mL (0.045 M) of dry CH_2Cl_2 were stirred together at room temperature for 30 min. The reaction mixture was then cooled to –78 °C and NIS (88 mg, 0.39 mmol) was added. The temperature of the reaction mixture was allowed to increase to –20 °C and then maintained at this temperature and stirred until the cyclization was complete (2.5 h), during this period, the progress of the reaction was monitored by TLC (EtOAc/hexane, 1:4). The reaction mixture was then cooled to –60 °C and AgOTf (13 mg, 0.052 mmol) was added. The reaction mixture was then stirred at –20 °C for a further 16 h. When the reaction was finished, triethylamine (1 mL) was added and the crude product was extracted with $NaHCO_3$/$Na_2S_2O_3$/CH_2Cl_2. The organic phase was dried with anhydrous $MgSO_4$. The crude product was purified by radial chromatography (from hexane to EtOAc/hexane, 1:3) to afford **22** (75 mg, 70%, α:β = 11:89) as a yellowish syrup. Spectroscopic data obtained from the α/β mixture. **22α**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.25 (m, 10 H), 5.35 (br. s, 1 H), 5.12 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H), 4.93–4.78 (m, $^3J_{H,H}$ = 10.0, 9.6 Hz, 4 H), 4.46 (dd, $^3J_{H,H}$ = 2.4, 4.4 Hz, 1 H), 4.36 (m, 1 H), 3.97 (dd, $^3J_{H,H}$ = 4.4, 3.0 Hz, 1 H), 3.76 (dd, $^3J_{H,H}$ = 3.0, 7.4 Hz, 1 H), 3.49–3.40 (m, 1 H), 2.41–0.66 (m, 44 H), 1.26 (m, 1 H) ppm. ^{13}C NMR (100.6 MHz, CDCl3): δ = 140.9, 140.5–138.6 (C_{Ar}), 128.7–126.9 (CH_{Ar}), 122.0, 99.5, 79.9, 78.0, 76.0, 75.8, 71.6,

65.4, 28.7 (C-I), 18.3 (C-6), 57.0–12.1 (24 C cholesterol) ppm. **22β**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.25 (m, 10 H), 5.35 (br. s, 1 H), 4.85 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 4.71–4.51 (m, $^3J_{H,H}$ = 12.0, 11.8 Hz, 4 H), 4.16 (dd, $^3J_{H,H}$ = 2.4, 2.0 Hz, 1 H), 4.08 (dq, $^3J_{H,H}$ = 9.2, 3.2 Hz, 1 H), 4.00 (dd, $^3J_{H,H}$ = 8.8, 2.4 Hz, 1 H), 3.49–3.40 (m, 1 H), 3.29 (dd, $^3J_{H,H}$ = 2.0, 9.2 Hz, 1 H), 2.41–0.66 (m, 44 H), 1.26 (m, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 140.9, 140.5–138.6 (C_{Ar}), 128.7–126.9 (CH_{Ar}), 122.0, 98.9, 82.0, 79.9, 78.3, 72.5, 71.8, 69.4, 33.9 (C-I), 18.3 (C-6), 57.0–12.1 (24C Cholesterol) ppm. $C_{47}H_{67}IO_4$ (822.94): calcd. 68.60% C, 8.21% H. Found: 68.44% C, 8.20% H.

Cholesteryl 3,4-di-*O*-benzyl-2,6-dideoxy-α/β-D-*ribo*-pyranoside (23): A solution of **22** (15 mg, 0.018 mmol, 1 equiv.) (α:β 1:7), Bu_3SnH (15 μL, 0.055 mmol, 3 equiv.) and Et_3B (5 μL, 1 M in hexane, 0.005 mmol. 0.3 equiv.) in 0.2 mL of toluene (0.085 M) was stirred for 22 h at room temp. (reaction controlled by NMR). The reaction mixture was diluted with EtOAc (5 mL) and washed with $NaHCO_3$. The combined organic extracts were dried (anhydrous $MgSO_4$) and concentrated under reduced pressure. The crude product was purified by radial chromatography using 1:4 EtOAc/hexane as the eluent to afford compound **23** (10 mg, 79%) as a 11:89 anomeric mixture. Spectroscopic data obtained from the α/β mixture. **23β**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42–6.99 (m, 10 H), 5.36 (br. s, 1 H), 4.94 (dd, $^3J_{H,H}$ = 2.0, 9.6 Hz, 1 H), 4.68 (s, 2 H), 4.55 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H), 4.39 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H), 4.02–3.97 (m, 2 H), 3.57–3.51 (m, 1 H), 3.12 (dd, $^3J_{H,H}$ = 2.6, 9.2 Hz, 1 H, 1 H), 2.33–0.65 (m, 44 H), 2.14 (ddd, $^3J_{H,H}$ = 2.0, 3.2, 13.6 Hz, 1 H), 1.55 (m, 1 H), 1.27 (d, $^3J_{H,H}$ = 4.0 Hz) ppm. ^{13}C NMR (100.6 MHz, CDCl3): δ = 141.0, 138.9 (C_{Ar}), 138.2 (C_{Ar}), 128.6–127.8 (CH_{Ar}), 121.9, 96.0, 80.0, 78.0, 71.8, 71.5, 71.5, 69.1, 36.1 (C-I), 18.7 (C-6), 58.0–12.1 (24C cholesterol) ppm. $C_{47}H_{68}O_4$ (697.04): calcd. C 80.99, H 9.83; found C 80.88, H 9.75.

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[1] a) A. C. Weymouth-Wilson, *Nat. Prod. Rep.* **1997**, *14*, 99; b) H. P. Albrecht, *Cardiac Glycosides* in *Naturally Occurring Glycosides*, R. Ikan, Wiley, Chichester, **1999**; c) *Glycoconjugates: Composition, Structure and Function* (Eds.: H. J. Allen, E. C. Kisailus), Marcel Dekker, New York, **1992**.

[2] a) T. Amaya, D. Takahashi, H. Tanaka, T. Takahashi, *Angew. Chem. Int. Ed.* **2003**, *42*, 1833–1836; b) L. G. Green, S. V. Ley, *Carbohydrates in Chemistry and Biology*; Wiley, Chichester, **2000**; vol 1, ch. 17; c) K. M. Koeller, C. H. Wong, *Chem. Rev.* **2000**, *100*, 4465–4493; d) K. M. Koeller, C. H. Wong, *Glycobiology* **2000**, *10*, 1157–1169; e) S. J. Danishefsky, J. Y. Roberge, *Pure Appl. Chem.* **1995**, *67*, 1647–1662.

[3] a) A. Köver, M. I. Matheu, Y. Díaz, S. Castillón, *Arkivoc* **2007**, 364–379; b) M. A. Rodríguez, O. Boutureira, X. Arnés, M. I. Matheu, Y. Díaz, S. Castillón, *J. Org. Chem.* **2005**, *70*, 10297–10310; c) X. Arnés, Y. Díaz, S. Castillón, *Synlett* **2003**, 2143–2146.

[4] For glycosylation methods that involve the use of 2-iododeoxy glycosyl donors, see: a) T. B. Durham, W. R. Roush, *Org. Lett.* **2003**, *5*, 1871–1874; b) P. Y. Chong, W. R. Roush, *Org. Lett.* **2002**, *4*, 4523–4526; c) A. Kirschning, M. Jesberger, K.-U. Schöning, *Org. Lett.* **2001**, *3*, 3623–3626; d) F. E. McDonald, K. S. Reddy, Y. Díaz, *J. Am. Chem. Soc.* **2000**, *122*, 4304–4309; e) W. R. Roush, B. W. Gung, C. E. Bennett, *Org. Lett.* **1999**, *1*, 891–893; f) W. R. Roush, S. Narayan, C. E. Bennett, K. Briner, *Org. Lett.* **1999**, *1*, 895–897; g) W. R. Roush, S. Narayan, *Org. Lett.* **1999**, *1*, 899–902; h) W. R. Roush, C. E. Bennett, *J. Am. Chem. Soc.* **1999**, *121*, 3541–3542; i) A. Kirschning, *Eur. J. Org. Chem.* **1998**, 2267–2274.

[5] For a procedure of synthesis of glycosides involving a mercury-induced cyclization of enol ethers, see: F. Paquet, P. Sinaÿ, *Tetrahedron Lett.* **1984**, *25*, 3071–3074.

[6] The 2-deoxy-2-iodo-1-thiopyranosides are useful starting materials for preparing glycals of all configurations; O. Boutureira, M. A. Rodríguez, M. I. Matheu, Y. Díaz, S. Castillón, *Org. Lett.* **2006**, *8*, 673–675.

[7] a) F. R. Van Herden, R. Vlegaar, R. M. Horak, R. A. Learmonth, V. Maharaj, R. D. Whittal, WO 98/46243, **1998**. For recent natural products incorporating pregnane 2-deoxyoligosaccharides, see: b) A. Perrone, A. Paza, S. F. Ercolino, A. I. Hamed, L. Parente, C. Pizza, S. Piacente, *J. Nat. Prod.* **2006**, *69*, 50–54; c) H. Bai, W. Li, K. Koike, T. Satou, Y. Chen, T. Nikaido, *Tetrahedron* **2005**, *61*, 5797–5811.

[8] For a review about glycosylation of steroids, see: H. Pellisier, *Tetrahedron* **2004**, *60*, 5123–5162.

[9] For a discussion on the different reactivities of the *Z* and *E* alkenyl sulfides towards cyclization, see ref.[3]

[10] For reviews about synthesis of 2-deoxyglycosides, see: a) A. Kirschning, M. Jesberger, K.-U. Schöning, *Synthesis* **2001**, 507–540; b) A. Veyrières, in *Carbohydrates in Chemistry and Biology* (Eds.: B. Ernst, G. W. Hart, P. Sinaÿ), Wiley-VCH, Weinheim, **2000**, part I, vol. I, p. 367; c) C. H. Marzabadi, R. W. Franck, *Tetrahedron* **2000**, *56*, 8385–8417; d) J. C. Castro-Palomino, R. R. Schmidt, *Synlett* **1998**, 501–503; e) K. Toshima, K. Tatsuta, *Chem. Rev.* **1993**, *93*, 1503–1531.

[11] C. Papageorgiou, C. Benezra, *Tetrahedron Lett.* **1984**, *25*, 6041–6044.

[12] O. Kanie, Y. Ito, T. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 12073–12074.

[13] C. Ollivier, P. Renard, *Chem. Rev.* **2001**, *101*, 3415–3434.

[14] H. S. Jensen, G. Limberg, C. Pedersen, *Carbohydr. Res.* **1997**, *302*, 109–112.

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