First Glycosylation of Decarestrictine B and D: A Route to Hybrid Antibiotics

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Abstract: The naturally occurring ten-membered lactones decarestrictine B (**4**) and D (**5**), which lower cholesterol levels, were glycosylated with deoxygenated 2-selenoglycosyl acetates **7a**, **7b**, and glycal **10** (obtained from D-glucose), and glycal **13** (obtained from L-rhamnose). Depending on the glycosylation method employed, the triol decarestrictine D was glycosylated with a high degree of regioselectivity. A set of hybrid structures were yielded by O-deblocking and in most cases reductive removal of a halogen or a phenylselenyl group from C-2 of the glycosides **14a–f**, **20a**, **20b**, and **24**. These hybrids were subjected to preliminary biological tests in which the novel glycoconjugates **15d** and **15e** displayed DNA-binding properties.

Keywords: antibiotics · DNA recognition · glycosides · glycosylations · macrocycles

Introduction

The frequency of resistance to commonly utilized antiinfective drugs in bacterial pathogens is increasing at an alarming rate.[1] The construction of hybrid or composite antibiotics, among other strategies, is regarded as an important approach for the development of new therapeutic reagents. This concept is based upon the combination of structural fragments commonly found in different antibiotics within one molecule.[2] Apart from the traditional method of chemical synthesis,[3] various research groups have recently employed genetically engineered hybrid organisms with modified biosynthetic genes to achieve this goal.[4]

As part of ongoing synthetic and biosynthetic studies on glycoconjugates[5] we envisaged constructs that are composed of a biologically active nonglycosylated secondary metabolite (aglycons) and a deoxygenated glycan unit. As interesting sugar moieties we employed D-olivose (2,6-dideoxy-D-*arabino*-pyranose, **1**, R = H), L-rhodinose (2,3,6-trideoxy-L-*threo*-pyranose, **2**, R = H), and the disaccharide **3**, which is composed of **1** and **2** (Figure 1). These and other rare sugars are commonly found as constituents of angucycline antibiotics,[6] and to a lesser extent in macrolide antibiotics and anthracycline cytostatics. In all these examples the carbohydrate units are essential for biological activity.[7] Apart from governing the pharmacokinetics of a drug, deoxygenated sugars also serve as recognition elements for the DNA binding of natural products.[8, 9] In fact, the contribution of these oligosaccharides to the energetics and sequence specificity of preferentially minor-groove DNA binding are only beginning to be explored.[10]

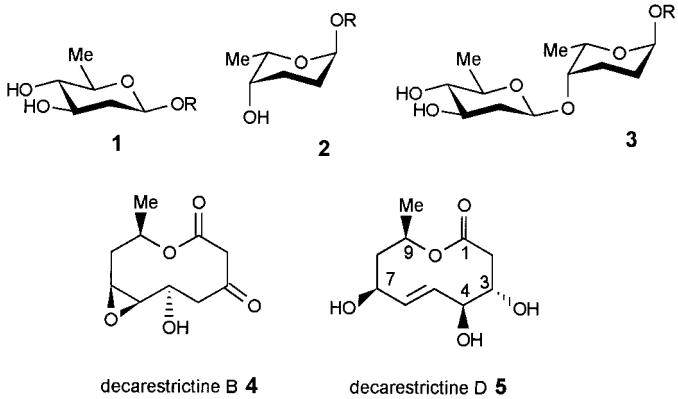

Figure 1. Deoxygenated glycosides derived from D-olivose and L-rhodinose and the ten-membered lactones decarestrictine B and D.

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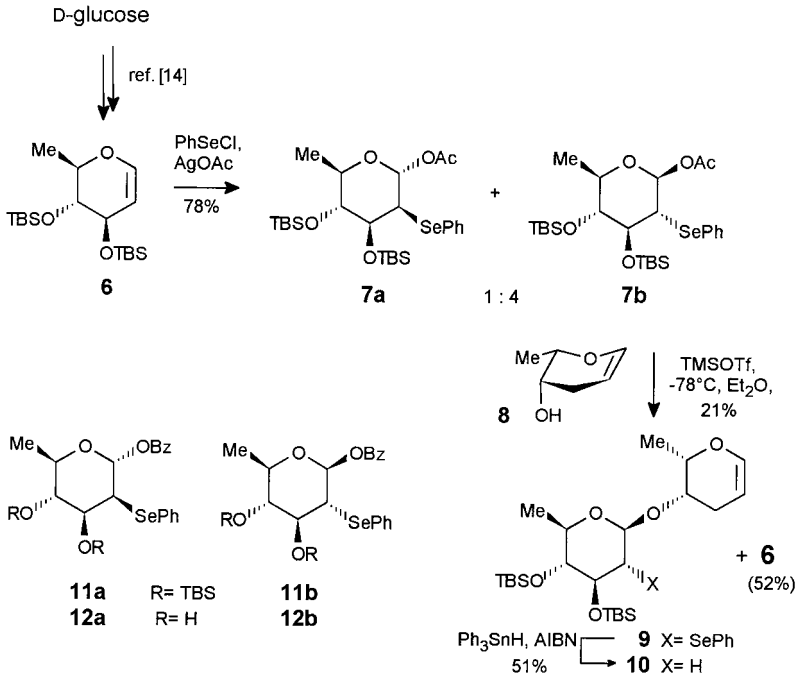
As aglycons we chose the ten-membered lactones decarestrictine B (**4**) and D (**5**). These are important new members of the growing class of ten-membered lactones of natural origin isolated from the fermentation broth of *Penicillium* species.[11] In particular **5** is the most potent in vivo inhibitor of the de novo cholesterol biosynthesis.[12] Although they have structural resemblance to aglycons with 12- and 14-membered macrolide antibiotics like methymycin and erythromycin A,[7] the decarestrictines do not exhibit antibacterial, antifungal, or antiviral activity. Therefore, combination of the ten-membered lactone moiety of the decarestrictines, which serves as an aglycon, with deoxygenated sugars would lead to hybrid antibiotics. Glycosylated structures derived from **4** and **5** are appealing, as a combination of two components of natural products from a bacterial and fungal source is achieved.



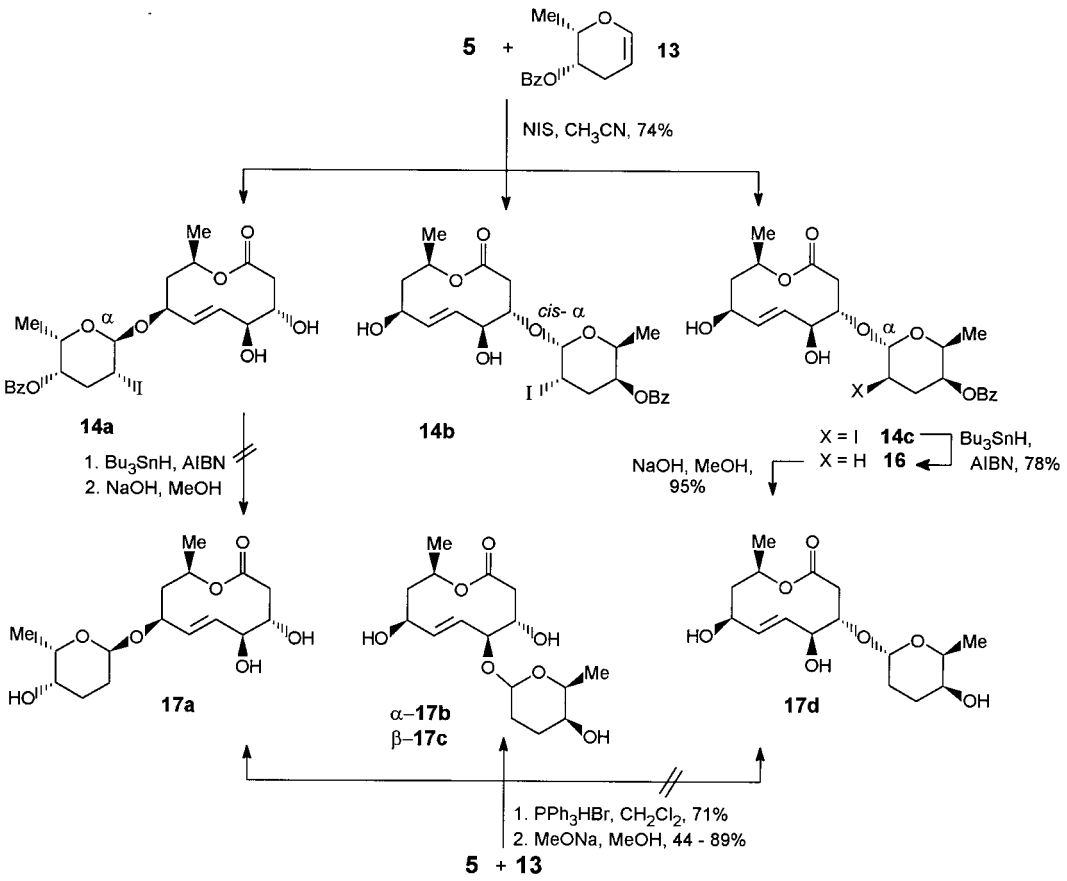
Scheme 1. Preparation of glycosyl donors **6**, **7**, **9**, and **10**.

Results and Discussion

Synthesis of glycosyl donors: In the first phase of the project, deoxysugars **1**–**3** had to be provided in sufficient amounts in an activated form. Glycals such as **6** and **8**, are ideally suited for this purpose as they can either be directly employed in glycosylation reactions to preferentially give α glycosides, or they may be transformed into alternative glycosyl donors that can give access to β glycosides.[10, 13] As shown in Scheme 1, the *tert*-butyldimethylsilyl-protected (TBS) 6-deoxy-D-glucal **6** was prepared from glucose by a known synthetic sequence.[14] To obtain a glycosyl donor suitable for the synthesis of β-glycosylated D-olivose, **6** was transformed into the seleno acetates **7a** and **b** following the procedure of Perez and Beau.[15] The isomers were isolated as a mixture (4:1 ratio) and were difficult to separate. As the ^{1}H NMR spectrum of the minor component **7a** showed a similar size for the diagnostic coupling constant $J_{1,2}$ as **7b** (5.8 Hz compared with 6.0 Hz), the mixture was coupled with benzyl alcohol in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) (yield: 85%). At this stage both stereoisomers **11a** and **b** were separated and desilylated (Bu_4NF, THF) to afford benzyl glycosides **12a** (94%) and **12b** (85%), respectively. With the large protective groups now removed, both isomers adopt a $^4C_1$(D) conformation that helped to unequivocally assign the configurations at C-1 and C-2. Coupling of **7a** and **7b** (4:1 mixture) with glycal **8**[16] at $-78\,^\circ$C with catalytic amounts of TMSOTf provided the labile disaccharide **9** in 21% yield along with 52% of glycal **6**, an indication of the well known reversibility for the addition of PhSeX to glycals.[15] In addition, the following observations are noteworthy. Only the β-isomer **7b** was glycosylated under the conditions employed. **7a** did not react and was reisolated in high purity. The acetoxy group in glycosyl acetate **7b** can be activated in the presence of another potential glycosyl donor group, such as the enolether double bond in **8**. The deselenylation of **9** by use of Ph_3SnH and azobisisobutyronitrile (AIBN) in refluxing toluene to generate the desired glycal **10**.

Abstract in German: *Die natürlich vorkommenden, den Cholesterinspiegel senkenden zehngliedrigen Lactone Decarestrictin B (**4**) und D (**5**) wurden mit den aus* D-*Glucose bzw.* L-*Rhamnose erhältlichen desoxygenierten 2-Seleno-glycosylacetaten **7a,b** sowie mit den Glycalen **10** und **13** glycosidisch verknüpft. In Abhängigkeit von der gewählten Glycosylierungsmethode konnte das Triol Decarestrictin D mit hoher Positionsselektivität glycosyliert werden. Nach Abspaltung der Schutzgruppen und in vielen Fällen reduktiver Entfernung von Halogen oder der Phenylselenyl-Gruppe an C-2 der Glycoside **14a–f**, **20a,b** und **24** wurden verschiedene Hybridstrukturen erhalten, die ersten biologischen Tests unterzogen wurden. Für die Bisglycoside **15d** und **15e** wurde DNA-Affinität gefunden.*

Glycosylation of decarestrictine D: In order to gain access to a diverse number of glycosylated products for pharmacological evaluation, and to assess the relative reactivity of hydroxy groups in polyhydroxylated decanolides, we employed unprotected decarestrictine D (**5**) for glycosylation reactions. The *N*-iodosuccinimide (NIS) method,[17] with **5**, 4-*O*-benzoylated L-rhodinal **13**,[16] and NIS in acetonitrile, afforded a mixture of mono- and bisglycosylated decanolides **14a–f** (11:2.2:4.5:4.5:1:1, 74%) with the expected preference for the α anomers (Scheme 2 and Figure 2). The ratio between monoglycosides **14a–c** and bisglycosides **14d–f** could be manipulated by changing of the molar ratio of **13** and **5**. The ratio of the isolated monoglycosylated products **14a**, **14b**, and **14c** (5:1:2) allowed us to deduce the relative reactivity and



Scheme 2. Glycosylations of decarestrictine D.

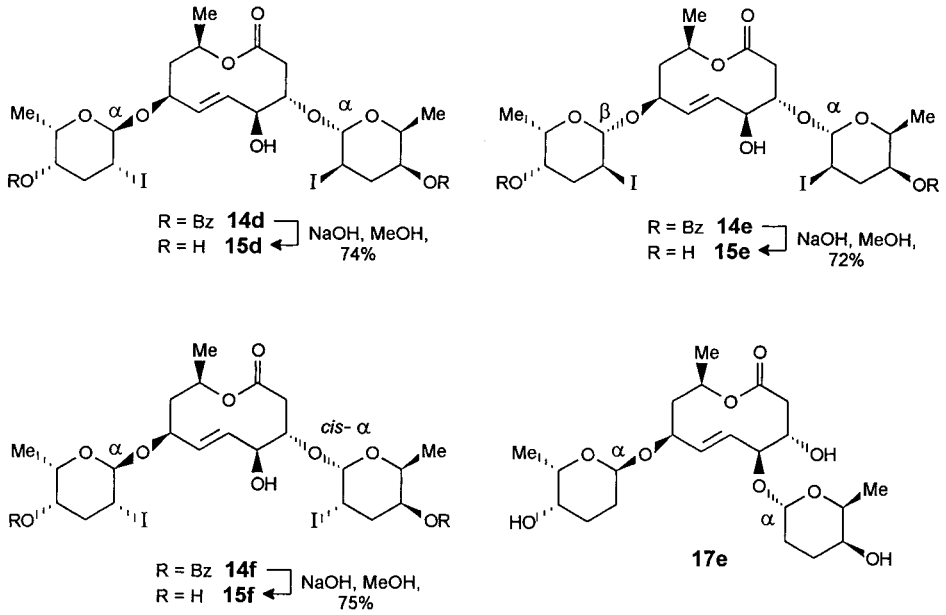


Figure 2. Bisglycosylated ten-membered lactones derived from decarestrictine D.

accessibility of the hydroxy groups of **5** in acetonitrile as 7-OH > 3-OH ≫ 4-OH. The same relative reactivity was also reflected in the formation of bisglycosides **14d–f**. Surprisingly, 1,2-*cis*-α-configurated adducts were exclusively found in rhodinosyl units of **14b** (^{1}H NMR: $^3J(1,2) = 2.8$, $^3J(2,3a) = 13.2$ Hz) and **14f** (^{1}H NMR: $^3J(1,2) = 2.8$, $^3J(2,3a) = 13.6$ Hz), which are both attached to 3-O of **5**. This result implies an anchimeric assistance by the lactone carbonyl group during the glycosylation process. Kessler et al. observed formation of these unexpected glycosylation products in the NIS-promoted synthesis of *O*-glycopeptides,[18] and encountered the high electron-donating power of benzyl-protecting groups in the glycal employed that favors the ring opening of the intermediate iodonium cation.

In contrast to Kessler's results, the benzoyl group should have an opposite effect here. Indeed, we could not detect any 3-*O*-1,2-*trans*-β-glycosides that would have further supported their explanation. Bu_3SnH-promoted deiodination of the regioisomer **14c** yielded **16**. In contrast, reductive exchange of iodine by hydrogen in **14a** led to stereoselective 5-*exo*-trigonal addition of the intermediate radical onto the olefinic double bond, thereby forming the highly substituted tetrahydrofuran **18** in excellent yield (88%, Scheme 3).[19] Also, utilization of the reducing system $NiCl_2 \cdot (H_2O)_6/NaBH_4$ could not suppress this ring closure. Debenzoylation of **14d–f** and **16** was achieved without substantial cleavage of the lactone ring under mildly basic reaction conditions to afford **15d–f** and **17d**.

In order to overcome these problems and to get a more efficient access to a wide number of glycosylated decarestrictines we turned our attention to a proton-induced glycosylation method.[20] Thus, activation of **13** by triphenylphosphane hydrobromide (TPHB), coupling with **5** in CH_2Cl_2 (71% yield), followed by debenzoylation furnished three monoglycosylated adducts **17a–c** and one bisglycoside **17e** (14:5.4:1:2) (Scheme 2).[21] Regioisomer **17d** was not detect-

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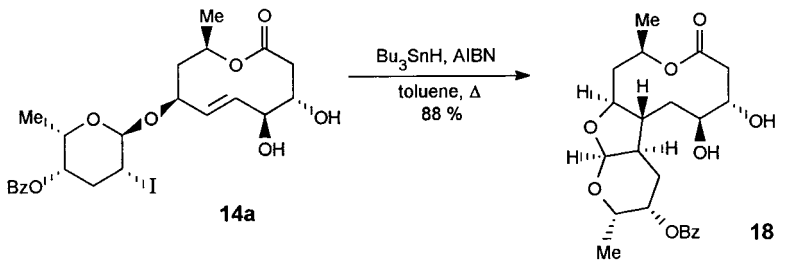


Scheme 3. Radical-induced cyclization of **14a**.

ed. This result clearly disclosed a reversed preference for the 3- and 4-OH groups in **5** compared with the NIS-method. This observation is further verified by formation of bisglycoside **17e**. The difference in regioselectivity can be rationalized on the basis of the difference of hydrogen-bonding capabilities and dielectric constants of the solvents employed. From conformational studies of **5** in crystalline form[22] as well as in solution it was concluded that the 3-OH group forms a strong hydrogen bond with the lactone carbonyl. This is reflected in the reactivity pattern of the proton-induced glycosylation procedure with CH_2Cl_2 as the solvent. In contrast, under iodonium induced glycosylation conditions the conformation of the half of the molecule containing the 3-OH group of **5** is altered, and the strong hydrogen bond was not detected; this can be rationalized in view of the larger polarity of acetonitrile compared with CH_2Cl_2.

The structures of all glycosylated products including **18** were comprehensively confirmed by detailed NMR experiments (COSY, HETCOR, NOESY, HMBC, and DQS). Acetylation of the remaining hydroxy groups followed by the study of the downfield shifts of adjacent C-bound protons in the ^{1}H NMR spectra further helped to locate the positions of glycosylation. Additional structural data were obtained by recording electrospray mass spectra (ESI-MS). Finally, by X-ray crystallographic analysis of **19**[23] the absolute configuration of the naturally occuring decarestrictine D was unequivocally established (Figure 3).[24]

Glycosylation of decarestrictine B: Decarestrictine B (**4**) possesses several structural features such as the oxirane ring and the acid–base sensitive β-ketoester functionality that have to be taken into consideration with respect to the glycosylation and subsequent deblocking reactions. From preliminary studies we knew that the benzoyl group, such as in **13**, cannot be removed from a sugar moiety that is attached to **4** without degradation of the decanolide framework.[25] To restrict the number of glycosylation products, we did not apply the NIS-methodology in this case. Instead, we used two glycosylation methods that are complementary as far as stereocontrol is concerned. Thus, when a 1:3 mixture of *O*-silylated glycals **7a** and **7b** was treated with 1.1 equiv of **4** (0.2 equiv, TMSOTf, $-78\,^\circ$C) the corresponding 2-phenylseleno-β-glycoside **20a** (89% with reference to **7b**), along with unreacted **7a** and **4**, was isolated (Scheme 4). Reductive removal of the phenylseleno substituent in **20a** under radical conditions provided **21a** in excellent yield. Finally, desilylation with tetrabutyl ammonium fluoride (TBAF) in dry THF afforded the desired hybrid structure **22a**. Likewise, pure **7a** (vide supra) was glycosylated with **4** at $-25\,^\circ$C with TMSOTf as promoter to afford **20b** in 92% yield. The target glycoside **22b** was eventually obtained in a two step sequence through the TBS-protected olivoside **21b**. In contrast, disaccharide **10** was coupled with **4** in the presence of a catalytic amount of Ph_3PHBr. The primary coupling product **24** turned out to be very labile and was immediately deblocked to generate glycoconjugate **25**. The synthetic strategy could not be reversed. When **9** was subjected to the glycosylation conditions in the presence of **4** the desired adduct **23** was detected by HRMS (calcd 842.3359, found 842.3359) in the crude product, but it completely decomposed upon attempted isolation.

Biological properties: Preliminary testing for the evaluation of the biological activity of these hybrids was conducted, and revealed DNA-binding activity for **5** and its bisglycosylated derivatives **15d** and **15e** by means of a new DNA-binding assay.[26] This assay works by the application of homogenized salmon sperma DNA [4 μg] and the test substance [5 μg] on an RP18 thin-layer chromatography (TLC) plate and determination of the altered R_f value after development of the chromatogram. The DNA binding of the substance is expressed as the quotient of the R_f in the presence of DNA (R_{f1}) and without DNA (R_{f2}); this results in $R_{f1}/R_{f2} = 0.1$ for **5** and **15d** and $R_{f1}/R_{f2} = 0.13$ for **15e**. All other glycosides including **4** showed no alterations in their R_f values under the influence of DNA. To further validate these results, we measured DNA melting curves of **5** and **15d**. The shift of the DNA melting points of **5** ($\Delta T_m = 0.7\,^\circ$C) and **15d** ($\Delta T_m = 0.8\,^\circ$C) proved DNA affinity and the stabilizing effect on DNA. In this context, it is worth noting that Schreiber et al.[27] proposed that the iodine group in the calicheamycin γ_1^I oligosaccharide binds to the exocyclic

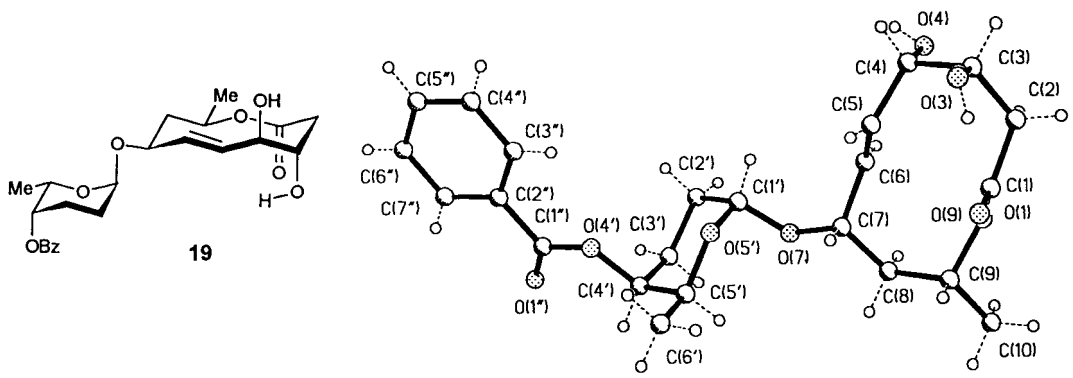
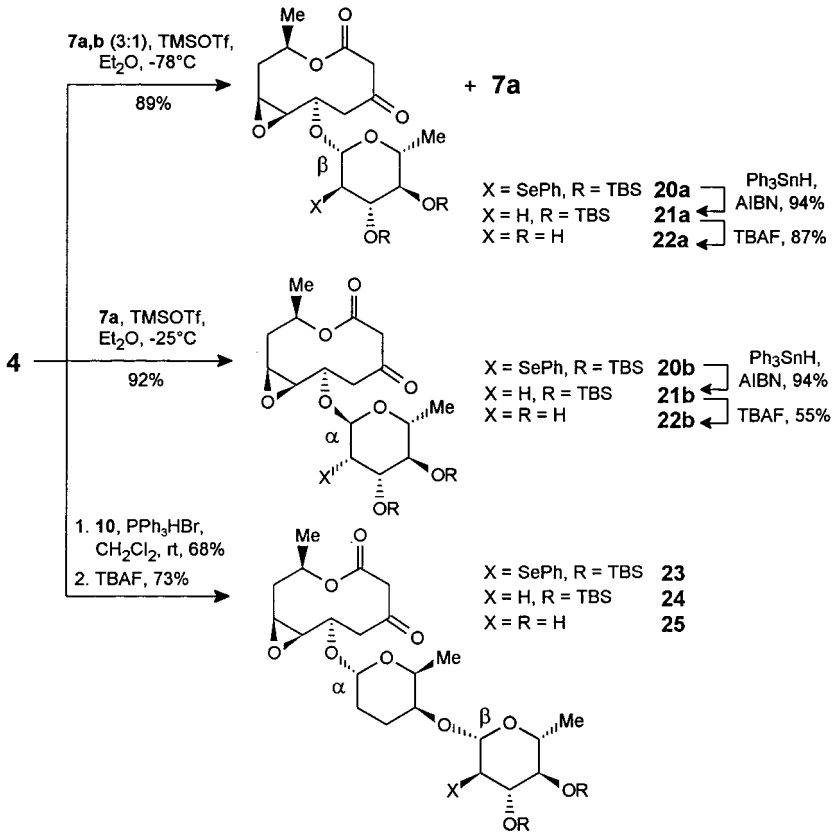


Figure 3. Structure of glycoside **19** in the crystal.



Scheme 4. Glycosylations of decarestrictine B.

amino group of guanine residues in duplex DNA; this was confirmed recently.[9, 28] In addition, Crothers et al. observed enhanced DNA affinity of daunomycin analogues that contain an iodo substituent in the sugar ring. Their data showed that much of the activity lost upon removing the charged amino group from the carbodrate framework can be compensated by an iodo substituent at C-2.[29] Further investigations on the DNA binding properties of decarestrictine D glycosides with a biosensor system[30] are in progress.

Experimental Section

General techniques: All temperatures quoted are uncorrected. Optical rotations: Perkin–Elmer 243b polarimeter. CD-spectra: Jasco J500A (given in $^{\circ}cm^2 \times 10^{-1} mol^{-1}$). ^1H NMR, ^{13}C NMR spectra: Bruker AMX300, ARX400, and Varian VXR500 spectrometer. ^{13}C NMR multiplicities: DEPT 135 method. Mass spectra: Finnigan MAT 95, 70 eV (EI-MS), and 200 eV (DCI-MS; NH_3). Unless otherwise stated, all reactions were run under a nitrogen atmosphere. All solvents used were of reagent grade and were further dried. Reactions were monitored by TLC on silica gel 60 PF^{254} (E. Merck, Darmstadt) and detected either by UV-absorption or by staining with H_2SO_4/4-methoxybenzaldehyde in ethanol. Preparative Column Chromatography: silica gel 60 (E. Merck, Darmstadt). Preparative HPLC: Abimed/Gilson. Glycal **6** was synthesized according to the literature,[14] while **8** and **13** have already been reported.[16]

1-*O*-Acetyl-3,4-bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-*α*-D-*manno*-pyranose (7a) and **1-*O*-Acetyl-3,4-bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-*β*-D-*gluco*-pyranose (7b)**: A solution of **6** (1.0 g, 2.79 mmol) in toluene (30 mL) was stirred at RT, and a small portion of powdered molecular sieves (4 Å), phenylselenyl chloride (0.69 g, 3.6 mmol), and silver(I) acetate (0.7 g, 4.2 mmol) was added. Stirring was continued at RT for 12 h and the reaction mixture was filtered. The resulting solution was concentrated in vacuo and purified by column chromatography (petroleum ether/EtOAc 6:1) to provide a 1:4 mixture of **7a** and **7b** (1.04 g, 1.81 mmol, 78%) as a colorless oil: Compound **7a**: physical and spectroscopic data are given below.

Compound **7b**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.63-7.58$ (m, 5H), 6.19 (d, $J = 6.0$ Hz, 1H), 4.16 (dd, $J = 4.4$, 2.8 Hz, 1H), 3.94 (dq, $J = 2.2$, 7.0 Hz, 1H), 3.59 (dd, $J = 4.4$, 2.2 Hz, 1H), 3.25 (dd, $J = 6.0$, 2.8 Hz, 1H), 1.88 (s, 3H), 1.39 (d, $J = 7.0$ Hz, 3H), 0.95, 0.92 (2s, 18H), 0.11, 0.10, 0.08 (3s, 12H); LRMS (DCI): *m/z* (%): 592.3 (1) $[M+NH_4^+]$, 532.3 (19), 515.2 (100); $C_{26}H_{46}O_5Si_2Se$: calcd C 54.43, H 8.08; found C 54.81, H 7.89.

Benzyl 3,4-bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-*α*-D-*manno*-pyranoside (11a) and **Benzyl 3,4-bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-*β*-D-*gluco*-pyranoside (11b)**: Freshly distilled benzyl alcohol (0.2 mL) was added to a solution of a 1:4 mixture of **7a** and **7b** (92 mg, 0.16 mmol) in diethyl ether (15 mL) at −78 °C, which was stirred. After 15 min, TMSOTf (43 μL, 1.5 equiv) in diethyl ether (1.5 mL) was added in small portions, and the reaction mixture was allowed to slowly warm to −25 °C until TLC (petroleum ether/EtOAc 20:1; $R_f = 0.32$) showed no further reaction. For the workup, saturated NH_4Cl solution was added, the phases were separated, and the aqueous phase extracted three times with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (petroleum ether/EtOAc 30:1) gave two fractions:

First fraction: **11a** (17.9 mg, 0.03 mmol, 18%); colorless oil; $[\alpha]_D^{24} = +41.8$ ($c = 1.01$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.53-7.17$ (m, 10H), 4.93 (d, $J = 4.0$ Hz, 1H), 4.71, 4.45 (2d, $J = 12.0$ Hz, 2H), 4.15 (dd, $J = 6.0$, 3.6 Hz, 1H), 3.77 (dq, $J = 7.0$, 6.4 Hz, 1H), 3.70 (dd, $J = 4.0$, 3.6 Hz, 1H), 3.49 (dd, $J = 7.0$, 6.0 Hz, 1H), 1.29 (d, $J = 6.4$ Hz, 3H), 0.93, 0.89 (2s, 18H), 0.16, 0.12, 0.11, 0.10 (4s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 137.9$, 133.6, 128.9, 128.4, 128.2, 127.8, 127.4, 127.1, 99.5, 75.8, 74.1, 70.8, 69.4, 50.8, 26.3, 26.0, 18.7, 18.4, 18.0, −3.2, −3.5, −4.1, −4.4; HRMS (EI) calcd for $C_{31}H_{50}O_4Si_2Se$ 622.2412, found 622.2412.

Second fraction: **11b** (67.6 mg, 0.11 mmol, 67%); colorless oil; $[\alpha]_D^{24} = -17.0$ ($c = 1.00$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.59-7.15$ (m, 10H), 4.99 (d, $J = 7.0$ Hz, 1H), 4.90, 4.57 (2d, $J = 11.8$ Hz, 2H), 4.20 (dd, $J = 4.4$, 2.4 Hz, 1H), 3.79 (dq, $J = 2.0$, 6.8 Hz, 1H), 3.56 (dd, $J = 4.4$, 2.0 Hz, 1H), 3.23 (dd, $J = 7.0$, 2.4 Hz, 1H), 1.42 (d, $J = 6.8$ Hz, 3H), 0.92, 0.87 (2s, 18H), 0.07, 0.06, 0.03 (3s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 137.7$, 133.5, 131.5, 128.8, 128.0, 127.9, 127.3, 129.6, 102.0, 77.5, 76.7, 74.7, 70.6, 49.6, 26.0, 25.9, 20.2, 18.1, 18.1, −4.2, −4.3, −4.4, −4.5; HRMS (EI) calcd for $C_{31}H_{50}O_4Si_2Se$ 622.2412, found 622.2412.

Benzyl 2,6-dideoxy-2-phenylseleno-*α*-D-*manno*-pyranoside (12a): TBAF·$3H_2O$ (39.8 mg, 0.13 mmol) was added to a solution of **11a** (8.9 mg, 0.014 mmol) in dry THF (2.0 mL) at RT. After 12 h, the reaction mixture was concentrated in vacuo. The semisolid residue was taken up with water and extracted three times with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (petroleum ether/EtOAc 4:1) afforded **12a** (5.3 mg, 0.013 mmol, 94%) as a colorless oil. $[\alpha]_D^{23} = +14.5^{\circ}$ ($c = 0.22$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.57-7.24$ (m, 10H), 5.31 (br s, 1H), 4.69, 4.47 (2d, $J = 11.6$ Hz, 2H), 4.05 (br ddd, $J = 9.6$, 9.4, 4.8 Hz, 1H), 3.77 (dq, $J = 9.0$, 6.2 Hz, 1H), 3.68 (dd, $J = 4.8$, 1.2 Hz, 1H), 3.17 (br dd, $J = 9.4$, 9.0 Hz, 1H), 2.49 (br d, $J = 9.6$ Hz, 1H, exchangeable), 2.49 (br s, 1H, exchangeable), 1.32 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 137.2$, 133.6, 129.8, 129.4, 128.5, 127.9, 127.9, 127.8, 100.7, 76.3, 70.4, 68.3, 69.4, 55.7, 17.6; HRMS (EI) calcd for $C_{19}H_{22}O_4Se$ 394.0683, found 394.0683; $C_{19}H_{22}O_4Se$: calcd C 58.02, H 5.64; found C 58.11, H 5.79.

Benzyl 2,6-dideoxy-2-phenylseleno-*β*-D-*gluco*-pyranoside (12b): TBAF·$3H_2O$ (43.5 mg, 0.14 mmol) was added to a solution of **11b** (28.4 mg,

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0.046 mmol) in dry THF (3 mL) at RT. After 30 min, the reaction mixture was worked up by the procedure described for **12a**. Flash chromatography (petroleum ether/EtOAc 10:1) afforded **12b** (15.3 mg, 0.039 mmol, 85%) as a colorless oil. $[\alpha]_D^{23} = -26.7^\circ$ ($c = 0.89$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.52-7.13$ (m, 10H), 4.91, 4.63 (d, $J = 12.0$ Hz, 1H), 4.39 (d, $J = 9.0$ Hz, 1H), 3.34–3.20 (m, 3H), 2.99 (dd, $J = 10.7$, 9.0 Hz, 1H), 3.77 (dq, $J = 9.0$, 6.2 Hz, 1H), 3.68 (dd, $J = 4.8$, 1.2 Hz, 1H), 3.17 (br dd, $J = 9.4$, 9.0 Hz, 1H), 2.49 (br d, $J = 9.4$ Hz, 1H, exchangeable), 2.49 (br s, 1H, exchangeable), 1.32 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 137.2$, 133.6, 129.8, 129.4, 128.5, 127.9, 127.9, 127.8, 100.7, 76.3, 70.4, 68.3, 69.4, 55.7, 17.6; HRMS (EI) calcd for $C_{19}H_{22}O_4Se$ 394.0683, found 394.0683; $C_{19}H_{22}O_4Se$: calcd C 58.02, H 5.64; found C 57.95, H 5.81.

4-*O*-[3,4-Bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-β-D-*gluco*-pyranosyl]-1,5-anhydro-2,3,6-trideoxy-L-*threo*-hex-1-enitol (9): A solution of a 1:3 mixture of **7a** and **7b** (220 mg, 0.383 mmol) in diethyl ether (15 mL) at −78 °C was stirred and **8** (≈70 mg, 0.61 mmol, in CH_2Cl_2) was added. After 15 min, TMSOTf (14 μL, 0.2 equiv) in diethyl ether (0.3 mL) was added and the solution was stirred for a further 5 min at ambient temperature. For the workup, saturated NH_4Cl solution was added, the phases separated, and the aqueous phase extratced three times with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (petroleum ether/EtOAc 20:1 followed by a second chromatographic step with petroleum ether/toluene 1:1) afforded **6** (60 mg, 0.2 mmol, 52%) and **9** (51 mg, 0.081 mmol, 21%) as colorless oils. $[\alpha]$ $\Theta_{217.0\,nm} = 13400^\circ$, $\Theta_{222.0\,nm} = 12900^\circ$, $\Theta_{237.4\,nm} = 16200^\circ$, $\Theta_{281.0\,nm} = -12100^\circ$, $\Theta_{349.2\,nm} = -362^\circ$ ($c = 0.0466$ mM in CH_3OH, 24 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (olivosyl) $\delta = 7.69-7.64$ and 7.31–7.24 (m, 5H), 5.05 (d, $J = 7.0$ Hz, 1H), 4.23 (dd, $J = 4.4$, 3.0 Hz, 1H), 3.82 (dq, $J = 2.2$, 6.8 Hz, 1H), 3.59 (dd, $J = 4.4$, 2.2 Hz, 1H), 3.24 (dd, $J = 7.0$, 3.0 Hz, 1H), 1.47 (d, $J = 6.8$ Hz, 3H), 0.99, 0.92 (2s, 18H), 0.15, 0.12, 0.10 (3s, 12H); (rhodinal) $\delta = 6.25$ (ddd, $J = 6.0$, 2.0, 2.0 Hz, 1H), 4.62 (ddd, $J = 6.0$, 4.4, 3.2 Hz, 1H), 4.13 (ddq, $J = 3.6$, 1.0, 6.6 Hz, 1H), 4.0 (ddd, $J = 7.8$, 5.8, 3.6 Hz, 1H), 2.34 (ddddd, $J = 16.8$, 5.8, 4.4, 2.0, 1.0 Hz, 1H), 2.18 (dddd, $J = 16.8$, 7.8, 3.2, 2.0 Hz, 1H), 1.23 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): (olivosyl) $\delta = 133.0$, 131.7, 128.8, 126.9, 102.8, 77.7, 76.7, 74.7, 49.8, 26.0, 25.9, 20.3, 18.1, 18.0, −4.2, −4.3, −4.4; (rhodinal) $\delta = 141.4$, 97.6, 73.2, 70.9, 25.3, 13.3; HRMS (EI) calcd for $C_{30}H_{52}O_5Si_2Se$ 628.2518, found 628.2518; $C_{30}H_{52}O_5Si_2Se$: calcd C 57.39, H 8.35; found C 57.31, H 8.45.

4-*O*-[3,4-Bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-β-D-*arabino*-pyranosyl]-1,5-anhydro-2,3,6-trideoxy-L-*threo*-hex-1-enitol (10): Compound **9** (21.5 mg, 0.034 mmol) and triphenyltin hydride (18 mg, 0.051 mmol) were mixed and dried in vacuo for 1 h. Dry toluene (4 mL) and a catalytic amount of AIBN were added, and the reaction mixture was refluxed in a preheated oil bath at 120 °C. This temperature was maintained for 2 h, then the mixture was cooled to RT and evaporated in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 1:1) afforded **10** (8.3 mg, 0.018 mmol, 51%) as a labile, colorless oil. $[\alpha]$ $\Theta_{319.2\,nm} = -110^\circ$, $\Theta_{452.6\,nm} = 25.7^\circ$ ($c = 0.0402$ mM in CH_3OH, 23 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (olivosyl) $\delta = 4.53$ (dd, $J = 9.8$, 2.0 Hz, 1H), 3.60 (ddd, $J = 11.4$, 7.8, 5.0 Hz, 1H), 3.20 (dq, $J = 8.8$, 6.0 Hz, 1H), 3.14 (dd, $J = 8.8$, 7.8 Hz, 1H), 2.13 (ddd, $J = 12.8$, 5.0, 2.0 Hz, 1H), 1.64 (ddd, $J = 12.6$, 11.4, 9.8 Hz, 1H), 1.23 (d, $J = 6.6$ Hz, 3H), 0.90, 0.89 (2s, 18H), 0.09, 0.08, 0.07 (3s, 12H); (rhodinal) $\delta = 6.28$ (ddd, $J = 6.0$, 2.0, 2.0 Hz, 1H), 4.61 (ddd, $J = 6.0$, 3.6, 3.6 Hz, 1H), 4.08 (dq, $J = 2.8$, 6.6 Hz, 1H), 3.89 (ddd, $J = 5.6$, 5.6, 2.8 Hz, 1H), 2.40–2.14 (m, 2H), 1.23 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): (olivosyl) $\delta = 97.8$, 77.7, 73.2, 72.7, 41.0, 26.3, 26.1, 18.7, 18.3, 18.0, −2.7, −3.0, −3.9, −4.1; (rhodinal) $\delta = 142.1$, 100.1, 73.6, 71.3, 26.1, 14.6; LRMS (DCI): *m/z* (%): 490.4 (100) $[M+NH_4^+]$, 376.4 (76).

NIS-promoted glycosylation of decarestrictine D: A suspension of **5** (577 mg, 2.67 mmol), **13** (388 mg, 1.780 mmol), and molecular sieves (3 Å, 0.2 g) in dry acetonitrile (50 mL) at 0 °C in the dark was stirred and three portions of NIS (521 mg, 2.314 mmol; freshly recrystallized from dioxane/CCl_4) were added over a period of 6 h. The reaction mixture was allowed to warm to RT within the next 12 h. For the workup, saturated $Na_2S_2O_3$ solution was added, the phases separated, and the aqueous phase extracted four times with EtOAc. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. Gradient column chromatography (silica gel, petroleum ether/EtOAc 10:1 to EtOAc) afforded three fractions ($R_f = 0.66$, $R_f = 0.38-0.28$, $R_f = 0.15$; petroleum ether/EtOAc 1:1). The first fraction was purified again by column chromatography (toluene/EtOAc 6:1)to afford **14d–14f** as pure materials. Likewise, the second fraction yielded **14a** and **14b** (toluene/EtOAc 1.5:1), while the third fraction gave **14c** (toluene/EtOAc 2:1) after column chromatography. The total yield of all isolated products was 74%.

*7-(4-*O*-Benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-lyxo-pyranosyloxy)-decarestrictine D (**14a**)*: (337 mg, 0.601 mmol, 34%) amorphous, colorless solid, m.p. 74 °C; $R_f = 0.38$ (silica gel, petroleum ether/EtOAc 1:1); $[\alpha]_D^{20.5} = -122.0^\circ$ ($c = 1.08$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.95$ (dd, $J = 15.8$, 2.5 Hz, 1H), 5.81 (ddd, $J = 15.8$, 9.7, 1.3 Hz, 1H), 5.30 (ddq, $J = 9.4$, 3.6, 6.2 Hz, 1H), 4.65 (br d, $J = 8.4$ Hz, 1H, exchangeable), 4.47 (m, 1H), 4.15 (ddd, $J = 9.7$, 7.6, 2.4 Hz, 1H), 4.07 (m, 1H), 2.65 (dd, $J = 14.2$, 1.8 Hz, 1H), 2.42 (br s, 1H, exchangeable), 2.41 (dd, $J = 14.2$, 6.1 Hz, 1H), 1.97–1.88 (m, 2H), 1.27 (d, $J = 6.2$ Hz, 3H); (rhodinosyl) $\delta = 8.24-7.44$ (m, 5H), 5.16 (br s, 1H), 5.13 (ddd, $J = 4.6$, 3.6, 2.2 Hz, 1H), 4.21 (dq, $J = 2.2$, 6.6 Hz, 1H), 4.07 (m, 1H), 2.82 (ddd, $J = 15.8$, 4.6, 4.6 Hz, 1H), 2.51 (ddd, $J = 15.8$, 3.6, 3.6 Hz, 1H), 1.28 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 174.9$, 133.3, 130.5, 75.4, 73.7, 72.2, 68.0, 41.2, 33.1, 21.2; (rhodinosyl) $\delta = 166.0$, 133.1, 130.3, 128.6, 128.3, 97.0, 67.9, 65.2, 31.9, 17.5, 16.2; LRMS (ES): *m/z* (%): 560.8 (88) $[M+H^+]$.

*3-(4-*O*-Benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-xylo-pyranosyloxy)-decarestrictine D (**14b**)*: (65 mg, 0.116 mmol, 6.5%) semisolid; $R_f = 0.28$ (silica gel, petroleum ether/EtOAc 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.92$ (ddd, $J = 16.4$, 8.8 Hz, 1H), 5.84 (dd, $J = 16.4$, 4.8 Hz, 1H), 5.19 (ddq, $J = 11.2$, 1.4, 6.4 Hz, 1H), 4.34 (m, 1H), 4.21 (ddd, $J = 11.2$, 8.8, 3.4 Hz, 1H), 3.92 (ddd, $J = 9.4$, 6.8, 3.4 Hz, 1H), 2.86 (dd, $J = 14.0$, 3.4 Hz, 1H), 2.36 (dd, $J = 14.0$, 9.4 Hz, 1H), 1.87 (br s, 1H, exchangeable), 1.86 (ddd, $J = 14.0$, 3.4, 1.4 Hz, 1H), 1.70 (br s, 1H, exchangeable), 1.75 (ddd, $J = 14.0$, 11.2, 11.2 Hz, 1H), 1.23 (d, $J = 6.4$ Hz, 3H); (rhodinosyl) $\delta = 8.08-7.44$ (m, 5H), 5.11 (d, $J = 2.8$ Hz, 1H), 5.0 (m, 1H), 4.49 (ddd, $J = 13.2$, 4.4, 2.8 Hz, 1H), 4.43 (br q, $J = 6.6$ Hz, 1H), 2.76 (ddd, $J = 14.0$, 13.2, 2.4 Hz, 1H), 2.49 (ddd, $J = 14.0$, 4.4, 2.8 Hz, 1H), 1.11 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 169.9$, 137.6, 126.7, 84.4, 72.8, 71.1, 68.3, 42.0, 37.0, 21.5; (rhodinosyl) $\delta = 165.7$, 133.4, 129.8, 128.5, 100.6, 72.3, 65.4, 35.7, 22.3, 16.7; LRMS (ES): *m/z* (%):560.8 (27) $[M+H^+]$.

*3-(4-*O*-Benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-lyxo-pyranosyloxy)-decarestrictine D (**14c**)*: (136 mg, 0.243 mmol, 14%); colorless solid, m.p. 82 °C; $R_f = 0.15$ (silica gel, petroleum ether/EtOAc 1:1); $[\alpha]_D^{24} = -60.5^\circ$ ($c = 1.02$ in $CHCl_3$); $[\alpha]$ $\Theta_{221.2\,nm} = -11900^\circ$, $\Theta_{242.5\,nm} = +932^\circ$, $\Theta_{269.8\,nm} = -2290^\circ$ ($c = 0.0621$ mM in MeOH, 25 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.92$ (ddd, $J = 16.3$, 9.2, 1.0 Hz, 1H), 5.79 (dd, $J = 16.3$, 4.2 Hz, 1H), 5.18 (ddq, $J = 11.0$, 1.8, 6.4 Hz, 1H), 4.24 (br dd, $J = 6.6$, 4.2 Hz, 1H), 4.21 (ddd, $J = 11.0$, 9.2, 3.4 Hz, 1H), 3.96 (ddd, $J = 8.6$, 6.6, 3.6 Hz, 1H), 2.83 (dd, $J = 14.2$, 3.6 Hz, 1H), 2.67 (br s, 1H, exchangeable), 2.36 (dd, $J = 14.2$, 8.6 Hz, 1H), 2.10 (br s, 1H, exchangeable), 1.89 (ddd, $J = 14.0$, 3.4, 3.4 Hz, 1H), 1.77 (ddd, $J = 14.0$, 11.0, 11.0 Hz, 1H), 1.25 (d, $J = 6.4$ Hz, 3H); (rhodinosyl) $\delta = 8.19-7.16$ (m, 5H), 5.38 (d, $J = 3.4$ Hz, 1H), 5.20 (ddd, $J = 5.8$, 4.8, 2.8 Hz, 1H), 4.53 (dq, $J = 2.8$, 6.6 Hz, 1H), 4.18 (ddd, $J = 5.8$, 4.8, 3.4 Hz, 1H), 2.88 (ddd, $J = 15.3$, 4.8, 4.8 Hz, 1H), 2.49 (ddd, $J = 15.3$, 5.8, 5.8 Hz, 1H), 1.29 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.1$, 137.2, 127.0, 82.3, 72.7, 71.0, 68.1, 42.2, 36.9, 21.5; (rhodinosyl) $\delta = 165.9$, 133.2, 130.0, 128.4, 125.3, 103.6, 68.7, 66.1, 33.0, 18.2, 15.6; LRMS (ES): *m/z* (%): 1143.1 (42) $[2M+H^+]$, 582.9 (98) $[M+Na^+]$, 560.8 (17) $[M+H^+]$.

*3,7-Bis-(4-*O*-benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-lyxo-pyranosyloxy)-decarestrictine D (**14d**)*: (102 mg, 0.113 mmol, 13%) colorless solid, m.p. 95 °C; $R_f = 0.38$ (silica gel, toluene/EtOAc 6:1); $[\alpha]$ $\Theta_{216.4\,nm} = -9170^\circ$, $\Theta_{243.0\,nm} = +469^\circ$, $\Theta_{264.8\,nm} = -21100^\circ$ ($c = 0.0359$ mM in MeOH, 25 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.93$ (dd, $J = 16.0$, 3.8 Hz, 1H), 5.79 (ddd, $J = 16.0$, 9.2, 0.8 Hz, 1H), 5.27–5.19 (m, 2H), 4.32 (br dd, $J = 6.7$, 3.8 Hz, 1H), 4.20 (m, 1H), 3.98 (ddd, $J = 8.4$, 6.0, 3.4 Hz, 1H), 2.80 (dd, $J = 14.0$, 3.4 Hz, 1H), 2.40 (dd, $J = 14.0$, 8.4 Hz, 1H), 2.0 (br s, 1H, exchangeable), 1.90–1.82 (m, 2H), 1.26 (d, $J = 6.4$ Hz, 3H); (rhodinosyl A) $\delta = 8.24-7.16$ (m, 5H), 5.19 (d, $J = 3.2$ Hz, 1H), 5.27–5.19 (m, 1H), 4.57 (dq, $J = 2.8$, 6.6 Hz, 1H), 4.18 (ddd, $J = 5.2$, 5.2, 3.2 Hz, 1H), 2.89 (ddd, $J = 15.2$, 4.6, 4.6 Hz, 1H), 2.54–2.49 (m, 1H), 1.29 (d, $J = 6.6$ Hz, 3H); (rhodinosyl B) $\delta = 8.24-7.16$ (m, 5H), 5.19 (d, $J = 2.2$ Hz, 1H), 5.15 (ddd, $J = 4.4$, 3.4, 2.8 Hz, 1H), 4.22 (dq, $J = 2.4$, 6.6 Hz, 1H), 4.06 (ddd, $J = 4.6$, 3.8, 2.2 Hz, 1H), 2.82 (ddd, $J = 15.8$, 5.2, 4.4 Hz, 1H), 2.54–2.49 (m, 1H), 1.29 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.3$, 133.4, 131.0, 82.1, 76.0, 71.4, 68.9, 40.8, 36.5, 21.7; (rhodinosyl A) $\delta = 166.1$, 133.3–125.5, 104.0, 68.2, 66.2, 33.1, 18.0, 16.0; (rhodinosyl B) $\delta = 166.1$, 133.3–125.5, 97.6, 68.1, 65.4 32.2, 17.4, 16.5.

*3-(4-*O*-Benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-xylo-pyranosyloxy)-7-(4-*O*-benzoyl-2-iodo-2,3,6-trideoxy-β-*L*-lyxo-pyranosyloxy)-decarestrictine D* (**14e**): (25 mg, 0.028 mmol, 3.1 %) amorphous, colorless solid; $R_f = 0.27$ (silica gel, toluene/EtOAc 6:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 6.02$ (dd, $J = 16.0$, 9.4 Hz, 1H), 5.83 (dd, $J = 16.0$, 4.0 Hz, 1H), 5.21 (ddq, $J = 11.2$, 1.0, 6.8 Hz, 1H), 4.25 (br dd, $J = 6.5$, 4.0 Hz, 1H), 4.24 (ddd, $J = 11.2$, 9.4, 2.6 Hz, 1H), 3.97 (ddd, $J = 8.6$, 6.5, 3.5 Hz, 1H), 2.82 (dd, $J = 14.2$, 3.5 Hz, 1H), 2.37 (dd, $J = 14.2$, 8.7 Hz, 1H), 2.20 (br s, 1H; exchangable), 2.05 (ddd, $J = 14.0$, 2.6, 1.0 Hz, 1H), 1.87 (ddd, $J = 14.0$, 11.2, 11.2 Hz, 1H), 1.27 (d, $J = 6.8$ Hz, 3H); (rhodinosyl at 7-O) $\delta = 8.15 - 7.43$ (m, 1H), 4.87 (ddd, $J = 3.0$, 3.0, 0.8 Hz, 1H), 4.56 (d, $J = 9.0$ Hz, 1H), 4.18 (ddd, $J = 13.2$, 9.0, 4.5 Hz, 1H), 3.91 (dq, $J = 0.8$, 6.4 Hz, 1H), 2.78 (ddd, $J = 14.8$, 4.5, 3.0 Hz, 1H), 2.42 (ddd, $J = 14.8$, 13.2, 3.0 Hz, 1H), 1.21 (d, $J = 6.4$ Hz, 3H); (rhodinosyl at 3-O) $\delta = 8.15 - 7.43$ (m, 1H), 5.39 (d, $J = 3.3$ Hz, 1H), 5.19 (ddd, $J = 5.6$, 4.9, 2.8 Hz, 1H), 4.54 (dq, $J = 2.8$, 6.4 Hz, 1H), 4.19 (ddd, $J = 5.6$, 4.9, 3.3 Hz, 1H), 2.88 (ddd, $J = 15.6$, 4.9, 4.9 Hz, 1H), 2.50 (ddd, $J = 15.6$, 5.6, 5.6 Hz, 1H), 1.29 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.1$, 135.4, 127.5, 81.9, 81.1, 71.2, 68.0, 39.7, 37.0, 21.6; (rhodinosyl at 7-O) $\delta = 165.9$, 133.4 – 128.4, 103.6, 73.7, 71.5, 41.7, 24.8, 17.0; (rhodinosyl at 3-O) $\delta = 165.9$, 133.4 – 128.4, 103.1, 68.7, 66.1, 32.9, 18.0, 15.7.

*3-(4-*O*-Benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-xylo-pyranosyloxy)-7-(4-*O*-benzoyl-2-iodo-2,3,6-trideoxy-α-*L*-lyxo-pyranosyloxy)-decarestrictine D* (**14f**): (24 mg, 0.026 mmol, 3.0 %) semisolid; $R_f = 0.42$ (silica gel, toluene/EtOAc 6:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.99$ (dd, $J = 15.8$, 4.0 Hz, 1H), 5.83 (dd, $J = 15.8$, 9.4 Hz, 1H), 5.25 (m, 1H), 4.46 (br dd, $J = 6.6$, 4.0 Hz, 1H), 4.23 (m, 1H), 3.96 (ddd, $J = 8.6$, 6.6, 3.2 Hz, 1H), 2.86 (dd, $J = 14.0$, 3.2 Hz, 1H), 2.74 (br s, 1H; exchangable), 2.41 (dd, $J = 14.0$, 8.6 Hz, 1H), 1.90 – 1.85 (m, 2H), 1.27 (d, $J = 6.6$ Hz, 3H); (rhodinosyl at 7-O) $\delta = 8.25 - 7.41$ (m, 10H), 5.21 (br s, 1H), 5.14 (br dd, $J = 6.2$, 3.8 Hz, 1H), 4.23 (dq, $J = 2.0$, 6.8 Hz, 1H), 4.05 (ddd, $J = 4.4$, 3.8, 2.0 Hz, 1H), 2.82 (ddd, $J = 15.4$, 4.4, 3.8 Hz, 1H), 2.55 – 2.48 (m, 2H), 1.29 (d, $J = 6.8$ Hz, 3H); (rhodinosyl at 3-O) $\delta = 8.25 - 7.41$ (m, 10H), 5.12 (br d, $J = 2.8$ Hz, 1H), 5.04 (m, 1H), 4.55 (br q, $J = 6.6$ Hz, 1H), 4.51 (ddd, $J = 13.6$, 4.6, 2.8 Hz, 1H), 2.81 (ddd, $J = 13.6$, 13.6, 2.6 Hz, 1H), 2.55 – 2.48 (m, 1H), 1.14 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.0$, 130.3, 129.0, 83.7, 75.9, 71.1, 68.1, 40.5, 36.4, 22.2; (rhodinosyl at 7-O) $\delta = 166.0$, 133.4 – 125.3, 97.4, 68.1, 65.4, 32.0, 17.3, 16.3; (rhodinosyl at 3-O) $\delta = 165.7$, 133.4 – 125.3, 100.8, 72.4, 65.2, 35.7, 21.5, 16.7.

3-(4-*O*-Benzoyl-2,3,6-trideoxy-α-L-*threo*-pyranosyloxy)-decarestrictine D (**16**): A catalytic amount of AIBN was added to a solution of **14c** (121 mg, 0.216 mmol) and tributyltin hydride (65 μL, 0.241 mmol) in toluene (50 mL), which was stirred, and the reaction mixture was heated at 50 °C for 19 h. After cooling, the reaction mixture was evaporated in vacuo and purified by column chromatography (petroleum ether/EtOAc 1:1) to afford **16** (73 mg, 0.168 mmol, 78 %) as an oil. $R_f = 0.13$ (silica gel, petroleum ether/EtOAc 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.90$ (dd, $J = 16.3$, 8.7 Hz, 1H), 5.82 (dd, $J = 16.3$, 4.1 Hz, 1H), 5.19 (ddq, $J = 10.8$, 1.5, 6.4 Hz, 1H), 4.22 (ddd, $J = 10.8$, 8.7, 3.6 Hz, 1H), 4.19 (dd, $J = 6.6$, 4.1 Hz, 1H), 3.98 (ddd, $J = 8.8$, 6.6, 3.6 Hz, 1H), 2.86 (dd, $J = 13.8$, 3.6 Hz, 1H), 2.36 (dd, $J = 13.8$, 8.8 Hz, 1H), 2.32, 1.84 (br s, 2H; exchangable), 1.89 (ddd, $J = 13.7$, 3.6, 1.5 Hz, 1H), 1.77 (ddd, $J = 13.7$, 11.0, 11.0 Hz, 1H), 1.24 (d, $J = 6.4$ Hz, 3H); (rhodinosyl) $\delta = 8.12 - 7.44$ (m, 5H; OBz), 5.16 (m, 1H), 5.09 (br s, 1H), 4.36 (br q, $J = 6.4$ Hz, 1H), 2.23 (dddd, $J = 13.6$, 13.6, 4.0, 2.8 Hz, 1H), 2.06 (dddd, $J = 13.8$, 13.8, 4.0, 4.0 Hz, 1H), 1.97 (dddd, $J = 13.6$, 3.1, 3.1, 3.1 Hz, 1H), 1.69 (br ddd, $J = 13.8$, 3.0, 3.0 Hz, 1H), 1.17 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.3$, 137.0, 127.3, 82.1, 72.8, 71.1, 67.9, 42.2, 37.0, 21.5; (rhodinosyl) $\delta = 166.1$, 133.0 – 128.4, 99.5, 70.0, 66.0, 24.8, 23.0, 17.2; LRMS (DCI): *m/z* (%): 452.5 (100) $[M+NH_4^+]$, 234.2 (14), 220.3 (25).

(1a*R*, 2*S*, 3*S*, 4a*R*, 4b*R*, 6*S*, 7*S*, 11*R*, 12a*S*)-3-Benzoyloxy-6,7-dihydroxy-2,11-dimethyl-dodecahydro-1,13-dioxacyclodeca[a]inden-9-one (**18**): A catalytic amount of AIBN was added to a solution of **14a** (393 mg, 0.701 mmol) and tributyltin hydride (213 μL, 0.77 mmol) in toluene (50 mL), which was stirred, and the reaction mixture was heated at 50 °C for 19 h. After cooling, the reaction mixture was evaporated in vacuo and washed twice with petroleum ether. Purification by column chromatography (petroleum ether/EtOAc 3.5:1) afforded **18** (267 mg, 0.614 mmol, 88 %) as a colorless solid. M.p. 81 °C; $R_f = 0.17$ (silica gel, petroleum ether/EtOAc 1:1); $[\alpha]$ $\Theta_{208.4\,nm} = -390°$, $\Theta_{227.3\,nm} = -1230°$ ($c = 0.087$ mM in MeOH, 22 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (decanolide) $\delta = 5.11$ (ddq, $J = 11.6$, 2.0, 6.0 Hz, 1H), 4.25 (ddd, $J = 11.6$, 4.6, 3.6 Hz, 1H), 3.56 (m, 1H), 3.44 (ddd, $J = 10.8$, 5.2, 2.0 Hz, 1H), 2.85 (dd, $J = 16.4$, 3.6 Hz, 1H), 2.36 (dd, $J = 16.4$, 11.6 Hz, 1H), 2.19 (ddd, $J = 14.0$, 2.0, 2.0 Hz, 1H), 2.15 and 1.95 (2br s, 2H, exchangeable), 1.96 (m, 2H), 1.91 (ddd, $J = 14.0$, 11.6, 10.8 Hz, 1H), 1.32 (d, $J = 6.0$ Hz, 3H), 1.23 (m, 1H); (pyran) $\delta = 8.08 - 7.43$ (m, 5H), 5.21 (d, $J = 4.1$ Hz, 1H), 5.07 (ddd, $J = 4.8$, 3.0, 1.6 Hz, 1H), 4.22 (dq, $J = 1.6$, 6.4 Hz, 1H), 2.31 (ddd, $J = 14.0$, 6.2, 4.8 Hz, 1H), 2.08 (dddd, $J = 10.8$, 6.2, 4.1, 1.5 Hz, 1H), 1.82 (ddd, $J = 14.0$, 10.8, 3.0 Hz, 1H), 1.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (decanolide) $\delta = 169.4$, 81.1, 74.7, 70.1, 68.6, 45.2, 43.2, 40.4, 37.5, 21.0; (pyran) $\delta = 166.2$, 133.2, 130.1, 129.7, 128.5, 99.0, 69.2, 67.3, 40.5, 30.2, 16.7; $C_{23}H_{30}O_8$ (434.49): calcd C 63.58, H 6.96; found C 63.60, H 6.89.

3-(2,3,6-Trideoxy-α-L-*threo*-pyranosyloxy)-decarestrictine D (**17d**): Debenzoylation of **16** (73 mg, 0.168 mmol) under standard conditions (NaOH, MeOH, molecular sieves 3 Å, RT, 24 h) afforded **17d** (53 mg, 0.160 mmol, 95 %) as a colorless solid. M.p. 56 °C; $R_f = 0.09$ (silica gel, EtOAc); $[\alpha]$ $\Theta_{200.0\,nm} = +2050°$, $\Theta_{223.9\,nm} = -406°$ ($c = 0.176$ mM in MeOH, 23 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.89$ (dd, 16.3, 8.8 Hz, 1H), 5.80 (dd, $J = 16.3$, 4.1 Hz, 1H), 5.17 (ddq, $J = 11.2$, 1.5, 6.4 Hz, 1H), 4.21 (ddd, $J = 12.0$, 8.7, 3.6 Hz, 1H), 4.16 (dd, $J = 6.8$, 4.1 Hz, 1H), 3.93 (ddd, $J = 9.1$, 6.8, 3.6 Hz, 1H), 2.84 (dd, $J = 13.7$, 3.6 Hz, 1H), 2.32 (dd, $J = 13.7$, 9.1 Hz, 1H), 2.24 (br s, 1H, exchangeable), 1.88 (ddd, $J = 13.8$, 3.6, 1.5 Hz, 1H), 1.84 (ddd, $J = 13.8$, 12.0, 11.2 Hz, 1H), 1.85 – 1.55 (br s, 1H, exchangeable), 1.24 (d, $J = 6.4$ Hz, 3H); (rhodinosyl) $\delta = 5.04$ (br d, $J = 2.0$ Hz, 1H), 4.18 (br q, $J = 6.6$ Hz, 1H), 3.63 (m, 1H), 2.09 (dddd, $J = 13.8$, 13.8, 3.8, 2.4 Hz, 1H), 1.99 (dddd, $J = 13.8$, 13.8, 3.8, 3.8 Hz, 1H), 1.85 (m, 1H), 1.85 – 1.55 (br s, 1H, exchangeable), 1.61 (m, 1H), 1.17 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.4$, 137.1, 127.3, 82.0, 72.9, 71.1, 68.0, 42.2, 37.0, 21.6; (rhodinosyl) $\delta = 99.6$, 67.3, 66.9, 25.7, 24.0, 17.1; LRMS (ES): *m/z* (%): 1139.0 (9.2), 1008.3 (29), 678.0 (49), 348.0 (100).

3,7-(2-Iodo-2,3,6-trideoxy-α-L-*xylo*-pyranosyloxy)-decarestrictine D (**15d**): Debenzoylation of **14d** (100 mg, 0.111 mmol) under standard conditions (NaOH, MeOH, molecular sieves 3 Å, RT, 24 h) afforded **15d** (57 mg, 0.082 mmol, 74 %) as a colorless solid. M.p. 66 °C; $R_f = 0.74$ (silica gel, CH_2Cl_2/CH_3OH 1:9); $[\alpha]$ $\Theta_{203.0\,nm} = +24\,300°$, $\Theta_{226.2\,nm} = -660°$, $\Theta_{244.6\,nm} = +115°$ ($c = 0.144$ mM in MeOH, 21 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.89$ (dd, $J = 16.1$, 3.9 Hz, 1H), 5.76 (ddd, $J = 16.1$, 9.4, 0.9 Hz, 1H), 5.20 (ddq, $J = 12.9$, 2.7, 6.5 Hz, 1H), 4.25 (ddd, $J = 6.0$, 3.9, 0.9 Hz, 1H), 4.15 (ddd, $J = 9.4$, 9.4, 5.0 Hz, 1H), 3.95 (ddd, $J = 8.8$, 6.0, 3.2 Hz, 1H), 2.78 (dd, $J = 14.0$, 3.2 Hz, 1H), 2.40 – 2.33 (m, 1H), 1.84 – 1.78 (m, 2H), 1.24 (d, $J = 6.5$ Hz, 3H); (rhodinosyl at 3-O) $\delta = 5.33$ (d, $J = 2.8$ Hz, 1H), 4.36 (dq, $J = 6.6$, 2.4 Hz, 1H), 4.12 (ddd, $J = 5.0$, 4.8, 2.8 Hz, 1H), 3.86 (ddd, $J = 4.8$, 4.8, 2.4 Hz, 1H), 2.74 (ddd, $J = 15.2$, 4.8, 4.8 Hz, 1H), 2.40 – 2.33 (m, 1H), 1.27 (d, $J = 6.6$ Hz, 3H); (rhodinosyl at 7-O) $\delta = 5.11$ (br s, 1H), 4.03 (dq, $J = 2.6$, 6.6 Hz, 1H), 3.99 (ddd, $J = 4.6$, 3.5, 0.9 Hz, 1H), 3.77 (ddd, $J = 4.5$, 3.9, 2.4 Hz, 1H), 2.67 (ddd, $J = 15.6$, 4.5, 4.5 Hz, 1H), 2.40 – 2.33 (m, 1H), 1.26 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.1$, 133.6, 130.7, 81.4, 75.8, 71.0, 67.9, 40.5, 36.3, 21.5; (rhodinosyl at 3-O) $\delta = 103.2$, 67.6, 67.6, 35.1, 20.2, 16.2; (rhodinosyl at 7-O) $\delta = 97.3$, 67.4, 66.7, 34.1, 20.0, 15.6; LRMS (DCI): *m/z* (%): 714.3 (100) $[M+NH_4^+]$, 474.2 (17), 242.1 (37), 234.2 (14).

3-(2-Iodo-2,3,6-trideoxy-α-L-*xylo*-pyranosyloxy)-7-(2-iodo-2,3,6-trideoxy-β-L-*xylo*-pyranosyloxy)-decarestrictine D (**15e**): Debenzoylation of **14e** (24.5 mg, 0.027 mmol) under standard conditions (NaOH, MeOH, molecular sieves 3 Å, RT, 24 h) afforded **15e** (13.5 mg, 0.019 mmol, 72 %) as a colorless solid. M.p. 98.5 °C; $R_f = 0.47$ (silica gel, EtOAc); $[\alpha]$ $\Theta_{219.8\,nm} = -13\,700°$, $\Theta_{244.6\,nm} = +282°$, $\Theta_{265.6\,nm} = -3820°$ ($c = 0.038$ mM in MeOH, 25 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.95$ (ddd, $J = 16.1$, 9.4, 0.8 Hz, 1H), 5.78 (dd, $J = 16.1$, 4.1 Hz, 1H), 5.17 (ddq, $J = 11.1$, 1.7, 6.4 Hz, 1H), 4.21 (ddd, $J = 6.4$, 4.1, 0.8 Hz, 1H), 4.17 (ddd, $J = 11.1$, 9.4, 3.0 Hz, 1H), 3.94 (ddd, $J = 8.6$, 6.4, 3.4 Hz, 1H), 2.78 (dd, $J = 14.1$, 3.4 Hz, 1H), 2.33 (dd, $J = 14.1$, 8.6 Hz, 1H), 2.01 (ddd, $J = 14.1$, 3.0, 1.7 Hz, 1H), 1.82 (ddd, $J = 14.1$, 11.0, 11.0 Hz, 1H), 1.25 (d, $J = 6.4$ Hz, 3H); (rhodinosyl at 7-O) $\delta = 4.50$ (d, $J = 9.0$ Hz, 1H), 4.15 (ddd, $J = 13.3$, 9.0, 4.9 Hz, 1H), 3.72 (dq, $J = 0.9$, 6.4 Hz, 1H), 3.38 (ddd, $J = 3.2$, 3.2, 0.9 Hz, 1H), 2.66 (ddd, $J = 14.0$, 4.9, 3.2 Hz, 1H), 2.24 (ddd, $J = 14.0$, 13.3, 2.8 Hz, 1H), 1.21 (d, $J = 6.4$ Hz, 3H); (rhodinosyl at 3-O) $\delta = 5.32$ (d, $J = 2.8$ Hz, 1H), 4.33 (dq, $J = 2.5$, 6.6 Hz, 1H), 4.13 (ddd, $J = 4.9$, 4.4, 2.8 Hz, 1H), 3.85 (ddd, $J = 4.9$, 4.5, 2.5 Hz, 1H), 2.72 (ddd, $J = 15.0$, 4.5, 4.5 Hz, 1H), 2.36 (ddd, $J = 15.0$, 4.9, 4.9 Hz, 1H), 1.27 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): (aglycon) $\delta = 170.2$, 135.4, 127.5, 81.7, 80.8, 71.2, 68.0, 39.7, 36.7, 21.5;

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(rhodinosyl at 7-O) δ 103.5, 74.8, 70.1, 44.5, 24.6, 16.9; (rhodinosyl at 3-O) $\delta = 103.2$, 67.7, 67.6, 35.0, 20.1, 15.6; LRMS (DCI): *m/z* (%): 714.3 (98) $[M+NH_4^+]$, 474.2 (13), 242.1 (40), 234.2 (11).

3-(2-Iodo-2,3,6-trideoxy-α-L-*xylo*-pyranosyloxy)-7-(2-iodo-2,3,6-trideoxy-α-L-*lyxo*-pyranosyloxy)-decarestrictine D (**15f**): Debenzoylation of **14f** (23.5 mg, 0.026 mmol) under standard conditions (NaOH, MeOH, molecular sieves 3 Å, RT, 24 h) afforded **15f** (13.6 mg, 0.02 mmol, 75%) as an amorphous, colorless solid. $R_f = 0.51$ (silica gel, EtOAc); $[\alpha]$ $\Theta_{202.2\,nm} = +9350^\circ$, $\Theta_{220.6\,nm} = -3140^\circ$, $\Theta_{239.8\,nm} = +1390^\circ$, $\Theta_{251.0\,nm} = +1790^\circ$ ($c = 0.144$ mM in MeOH, 22 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.94$ (dd, $J = 16.2$, 4.2 Hz, 1H), 5.79 (dd, $J = 16.2$, 9.2 Hz, 1H), 5.22 (ddq, $J = 8.8$, 4.0, 6.4 Hz, 1H), 4.37 (br dd, $J = 6.6$, 4.2 Hz, 1H), 4.17 (m, 1H), 3.90 (ddd, $J = 9.0$, 6.0, 3.5 Hz, 1H), 2.86 (dd, $J = 13.8$, 3.4 Hz, 1H), 2.40–2.33 (m, 1H), 1.86–1.78 (m, 2H), 1.25 (d, $J = 6.4$ Hz, 3H); (rhodinosyl at 7-O) $\delta = 5.13$ (br s, 1H), 4.04 (dq, $J = 2.0$, 6.6 Hz, 1H), 3.98 (ddd, $J = 4.6$, 3.6, 2.0 Hz, 1H), 3.77 (br dd, $J = 4.8$, 4.4 Hz, 1H), 2.70 (ddd, $J = 15.4$, 4.8, 4.4 Hz, 1H), 2.40–2.33 (m, 2H), 1.28 (d, $J = 6.6$ Hz, 3H); (rhodinosyl at 3-O) $\delta = 5.02$ (br d, $J = 3.0$, 1H), 4.56 (ddd, $J = 13.4$, 4.6, 3.0 Hz, 1H), 4.32 (br q, $J = 6.6$ Hz, 1H), 3.60 (ddd, $J = 3.8$, 2.6, 2.0 Hz, 1H), 2.64 (ddd, $J = 13.4$, 13.4, 2.6 Hz, 1H), 2.40–2.33 (m, 1H), 1.14 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 170.0$, 134.3, 130.0, 83.4, 76.1, 71.3, 68.1, 40.5, 29.7, 21.6; (rhodinosyl at 7-O) $\delta = 97.5$, 67.4, 66.8, 34.2, 19.9, 16.2; (rhodinosyl at 3-O) $\delta = 100.8$, 70.4, 66.3, 38.7, 22.6, 16.6; LRMS (DCI): *m/z* (%): 714.3 (100) $[M+NH_4^+]$, 474.2 (23), 242.1 (31), 234.2 (19).

PPh_3HBr-promoted glycosylation of decarestrictine D: A catalytic amount (5 mol%) of triphenylphosphane hydrobromide was added to a solution of **5** (252 mg, 1.17 mmol) and **13** (130 mg, 0.60 mmol) in dry dichloromethane (6 mL), and the reaction mixture was stirred for 3 h at RT. For the workup, it was washed with saturated $NaHCO_3$ solution (3 mL) and brine (3 mL), and the combined aqueous layers were extracted twice with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Gradient column chromatography (silica gel, petroleum ether/EtOAc 4:1 to 1:1) afforded four fractions ($R_f = 0.62$, $R_f = 0.36$, $R_f = 0.25$, $R_f = 0.15$; petroleum ether/EtOAc 1:1). The total yield of all isolated products (**19**) was 71%. The four compounds were purified to high purity and directly debenzoylated (**17**). This was achieved by employing Zemplén conditions (NaOMe/MeOH).[31]

*7-(4-*O*-Benzoyl-2,3,6-trideoxy-α-*L*-threo-pyranosyloxy)-decarestrictine D* (**19**): colorless solid, m.p. 84 °C; $R_f = 0.36$ (silica gel, petroleum ether/EtOAc 1:1); $[\alpha]$ $\Theta_{217.6\,nm} = -707^\circ$, $\Theta_{229.0nm} = 5420^\circ$, $\Theta_{253.2\,nm} = -831^\circ$ ($c = 0.130$ mM in MeOH, 22 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.95$ (dd, $J = 16.0$, 2.8 Hz, 1H), 5.76 (ddd, $J = 16.0$, 9.6, 1.0 Hz, 1H), 5.32 (ddq, $J = 12.2$, 0.8, 6.5 Hz, 1H), 4.62 (br d, $J = 8.8$ Hz, 1H; exchangable), 4.46 (dddd, $J = 4.0$, 3.4, 2.8, 1.0 Hz, 1H), 4.17 (ddd, $J = 9.6$, 6.4, 8.2 Hz, 1H), 4.05 (dddd, $J = 8.8$, 4.0, 6.5, 1.4 Hz, 1H), 2.64 (dd, $J = 14.2$, 1.4 Hz, 1H), 2.41 (dd, $J = 14.2$, 6.5 Hz, 1H), 1.94–1.90 (m, 2H), 1.77 (d, $J = 3.4$ Hz, 1H; exchangable), 1.28 (d, $J = 6.6$ Hz, 3H); (rhodinosyl) $\delta = 8.10$–7.40 (m, 5H), 5.05 (m, 1H), 4.98 (br d, $J = 2.6$ Hz, 1H), 4.08 (dq, $J = 1.0$, 6.6 Hz, 1H), 2.15 (dddd, $J = 13.4$, 13.4, 4.0, 3.0 Hz, 1H), 2.02 (dddd, $J = 13.6$, 13.4, 3.8, 3.8 Hz, 1H), 1.94–1.90 (m, 1H), 1.52 (br d, $J = 13.6$ Hz, 1H), 1.19 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 174.9$, 132.6, 132.3, 74.6, 73.8, 72.4, 68.4, 41.5, 33.2, 21.3; (rhodinosyl) $\delta = 166.2$, 133.1, 130.2, 129.8, 128.4, 92.6, 70.0, 65.5, 24.1, 23.0, 17.3; $C_{23}H_{30}O_8$ (434.49): calcd C 63.58, H 6.96; found C 63.73, H 6.79; Crystal structure data:[23] crystal dimensions $0.4 \times 0.4 \times 0.4$ mm, tetragonal, space group $P4_12_12$, $a = 10.552(10)$, $c = 40.902(6)$ Å, $Z = 8$, $V = 4554.2(9)$ Å^3, $\rho_{calcd} = 1.267$ g cm^{-3}, $Mo_{K\alpha}$ radiation, ($\lambda = 71.073$ pm), $T = 153(2)$ K, 3382 reflections, 2966 symmetry-independent reflections, $2\Theta_{max} = 45^\circ$, program SHELXTL, parameters = 284, $R^1 = 0.0848$ ($I > 2\sigma$) and $wR^2 = 0.1562$.

*7-(2,3,6-Trideoxy-α-*L*-threo-pyranosyloxy)-decarestrictine D* (**17a**): Debenzoylation of the second fraction ($R_f = 0.36$ vide supra, 116.3 mg, 0.268 mmol) under standard conditions[31] afforded **17a** (66.1 mg, 0.20 mmol, 75%) after flash chromatography (CH_2Cl_2/CH_3OH 9:1) as a colorless solid. M.p. 41 °C; $R_f = 0.08$ (silica gel, CH_2Cl_2/CH_3OH 9:1); $[\alpha]$ $\Theta_{201.5\,nm} = +539^\circ$, $\Theta_{209.1\,nm} = 0^\circ$, $\Theta_{218.3\,nm} = -585^\circ$ ($c = 0.303$ mM in MeOH, 21 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.90$ (dd, $J = 15.8$, 2.8 Hz, 1H), 5.73 (ddd, $J = 15.8$, 9.6, 1.2 Hz, 1H), 5.28 (ddq, $J = 9.6$, 3.2, 6.4 Hz, 1H), 4.63 (br s, 1H; exchangable), 4.11 (ddd, $J = 9.6$, 9.6, 5.2 Hz, 1H), 4.03 (ddd, $J = 6.4$, 4.0, 1.8 Hz, 1H), 2.62 (dd, $J = 14.2$, 1.8 Hz, 1H), 2.41 (br s, 1H; exchangable), 2.39 (dd, $J = 14.2$, 6.4 Hz, 1H), 1.90–1.86 (m, 2H), 1.26 (d, $J = 6.4$ Hz, 3H); (rhodinosyl) $\delta = 4.84$ (br d, $J = 2.0$ Hz, 1H), 3.92 (br q, $J = 6.8$ Hz, 1H), 3.57 (m, 1H), 1.98 (dddd, $J = 13.4$, 13.4, 3.8, 2.6 Hz, 1H), 1.96 (br s, 1H; exchangable), 1.91 (dddd, $J = 13.4$, 13.4, 3.8, 3.8 Hz, 1H), 1.74 (m, 1H), 1.43 (m, 1H), 1.18 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 174.9$, 132.1, 131.4, 74.6, 73.8, 72.3, 68.4, 41.4, 33.3, 21.3; (rhodinosyl) $\delta = 92.7$, 67.4, 66.4, 25.7, 23.3, 17.2; LRMS (ES): *m/z* (%): 678.0 (36), 348.0 (100).

*4-(2,3,6-Trideoxy-α-*L*-threo-pyranosyloxy)-decarestrictine D* (**17b**): Debenzoylation of the third fraction ($R_f = 0.25$ vide supra, 44.1 mg, 0.102 mmol) under standard conditions[31] afforded **17b** (14.7 mg, 0.2 mmol, 44%; contaminated with ≈30% of the 7-β-anomer, which could not be separated) after flash chromatography (EtOAc) as a semisolid oil. $R_f = 0.13$ (silica gel, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.91$ (ddd, $J = 15.8$, 9.2, 0.8 Hz, 1H), 5.81 (dd, $J = 15.8$, 2.8 Hz, 1H), 5.27 (ddq, $J = 11.0$, 1.6, 6.4 Hz, 1H), 4.61 (br s, 1H; exchangable), 4.37 (ddd, $J = 4.0$, 2.8, 0.8 Hz, 1H), 4.18 (ddd, $J = 10.6$, 9.2, 3.8 Hz, 1H), 4.06 (m, 1H), 2.56 (dd, $J = 14.2$, 1.8 Hz, 1H), 2.39 (dd, $J = 14.2$, 6.3 Hz, 1H), 1.93 (ddd, $J = 14.0$, 3.8, 1.6 Hz, 1H), 1.90–1.50 (br s, 1H; exchangable), 1.83 (ddd, $J = 14.0$, 11.0, 11.0 Hz, 1H), 1.25 (d, $J = 6.4$ Hz, 3H); (rhodinosyl) $\delta = 4.93$ (br d, $J = 2.8$ Hz, 1H), 3.95 (br q, $J = 6.6$ Hz, 1H), 3.59 (m, 1H), 2.08 (dddd, $J = 13.8$, 13.8, 4.0, 2.6 Hz, 1H), 1.99 (dddd, $J = 13.8$, 13.8, 3.8, 3.8 Hz, 1H), 1.90–1.50 (br s, 1H; exchangable), 1.79 (m, 1H), 1.56 (m, 1H), 1.12 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 174.9$, 134.2, 128.2, 74.8, 72.7, 71.5, 68.2, 42.0, 33.5, 21.3; (rhodinosyl) $\delta = 95.6$, 67.2, 66.9, 25.8, 23.6, 17.1; LRMS (ES): *m/z* (%):678.0 (21), 348.0 (100).

*4-(2,3,6-Trideoxy-β-*L*-threo-pyranosyloxy)-decarestrictine D* (**17c**): Debenzoylation of the fourth fraction ($R_f = 0.15$ vide supra, 8.2 mg, 0.019 mmol) under standard conditions[31] and chromatographic purification (CH_2Cl_2/CH_3OH 1:9) afforded **17c** (5.3 mg, 0.016 mmol, 84%) as a semisolid oil. $R_f = 0.18$ (silica gel, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.81$ (ddd, $J = 15.8$, 8.8, 0.6 Hz, 1H), 5.73 (dd, $J = 15.8$, 2.4 Hz, 1H), 5.26 (ddq, $J = 11.0$, 1.6, 6.2 Hz, 1H), 4.66 (br d, $J = 6.0$ Hz, 1H; exchangable), 4.45 (m, 1H), 4.20 (m, 1H), 4.19 (ddd, $J = 11.0$, 8.8, 3.8 Hz, 1H), 2.55 (dd, $J = 14.4$, 1.8 Hz, 1H), 2.39 (dd, $J = 14.4$, 6.6 Hz, 1H), 1.91 (ddd, $J = 13.8$, 2.8, 1.6 Hz, 1H), 1.82 (ddd, $J = 13.8$, 11.0, 11.0 Hz, 1H), 1.76–1.62 (br s, 1H; exchangable), 1.25 (d, $J = 6.2$ Hz, 3H); (rhodinosyl) $\delta = 4.45$ (dd, $J = 7.0$, 4.6 Hz, 1H), 3.57 (dq, $J = 0.6$, 6.4 Hz, 1H), 3.48 (m, 1H), 2.00 (dddd, $J = 13.4$, 2.8, 2.6, 2.6 Hz, 1H), 1.76–1.62 (m, 4H; 1H exchangable), 1.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 174.0$, 134.7, 127.7, 77.7, 73.2, 72.6, 68.0, 43.1, 33.9, 21.3; (rhodinosyl) $\delta = 101.0$, 74.0, 66.6, 29.8, 25.5, 17.1; LRMS (ES): *m/z* (%): 1139.0 (5.3), 1008.3 (33), 678.0 (51), 348.0 (100).

*4,7-Bis-(2,3,6-trideoxy-α-*L*-threo-pyranosyloxy)-decarestrictine D* (**17e**): Debenzoylation of the first fraction ($R_f = 0.62$ vide supra, 25.5 mg, 0.039 mmol) under standard conditions[31] and chromatographic purification with EtOAc afforded **17e** (15.5 mg, 0.035 mmol, 89%) as a colorless solid. M.p. 76 °C; $R_f = 0.10$ (silica gel, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.88$ (dd, $J = 15.8$, 3.0 Hz, 1H), 5.72 (ddd, $J = 15.8$, 9.6, 1.0 Hz, 1H), 5.31 (ddq, $J = 12.0$, 4.0, 6.4 Hz, 1H), 4.61 (br s, 1H; exchangable), 4.34 (ddd, $J = 4.0$, 3.0, 1.0 Hz, 1H), 4.10 (m, 1H), 4.01 (m, 1H), 2.57 (dd, $J = 14.2$, 1.8 Hz, 1H), 2.40 (dd, $J = 14.2$, 6.2 Hz, 1H), 1.91–1.86 (m, 2H), 1.27 (d, $J = 6.4$ Hz, 3H); (rhodinosyl at 7-O) $\delta = 4.80$ (br s, 1H), 3.93 (br q, $J = 6.6$ Hz, 1H), 3.58–3.55 (m, 1H), 2.09–2.00 (m, 1H), 2.00–1.91 (m, 2H; 1H exchangable), 1.82–1.76 (m, 1H), 1.42–1.37 (m, 1H), 1.19 (d, $J = 6.6$ Hz, 3H); (rhodinosyl at 4-O) $\delta = 4.84$ (br s, 1H), 3.92 (br q, $J = 6.6$ Hz, 1H), 3.58–3.55 (m, 1H), 2.09–2.00 (m, 1H), 2.00–1.91 (m, 2H; 1H exchangable), 1.82–1.76 (m, 1H), 1.59–1.54 (m, 1H), 1.09 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (aglycon) $\delta = 175.0$, 132.0, 130.6, 75.9, 74.5, 71.9, 68.4, 41.4, 33.5, 21.3; (rhodinosyl at 7-O) $\delta = 92.6$, 67.3, 66.3, 25.9, 23.6, 17.2; (rhodinosyl at 4-O) $\delta = 96.5$, 67.4, 67.0, 25.7, 23.4, 17.0; LRMS (DCI): *m/z* (%): 462.5 (100) $[M+NH_4^+]$.

5-[3,4-Bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-β-D-*gluco*-pyranosyloxy]-decarestrictine B (**20a**): A 1:3 mixture of **7a** and **7b** (162 mg, 0.282 mmol) was added to a solution of decarestrictine B (**4**) (67 mg, 0.313 mmol) in dry diethyl ether (10 mL) at −78 °C and the reaction was stirred. After 15 min TMSOTf (11.3 μL, 0.2 equiv) in diethyl ether (0.2 mL) was added and stirring was continued for 5 min at ambient temperature. For the workup, the reaction mixture was hydrolyzed with a saturated NH_4Cl solution and allowed to warm to RT. After washing three times with CH_2Cl_2, the combined organic phases were dried ($MgSO_4$) and

evaporated in vacuo. Flash chromatography (toluene/EtOAc 20:1) gave three fractions:

First fraction: **4** (25.4 mg, 0.119 mmol, 38% with reference to starting **4**).[12]

Second fraction: **7a** (33.3 mg; 0.058 mmol); colorless oil; $[\alpha]_D^{24.5} = +17.2$ ($c = 1$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.60-7.54$ (m, 2H), 7.33–7.24 (m, 3H), 6.17 (d, $J = 5.8$ Hz, 1H), 4.14 (dd, $J = 5.0$, 3.4 Hz, 1H), 3.83 (dq, $J = 6.2$, 6.6 Hz, 1H), 3.68 (dd, $J = 5.8$, 3.4 Hz, 1H), 3.53 (dd, $J = 6.2$, 5.0 Hz, 1H), 1.92 (s, 3H), 1.34 (d, $J = 6.6$ Hz, 3H), 0.94, 0.90 (2s, 18H), 0.16, 0.13, 0.12, 0.10 (4s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 169.5$, 133.8, 129.0, 127.4, 93.6, 74.9, 74.6, 73.5, 48.6, 26.1, 25.9, 21.0, 18.3, 18.2, 18.0, −3.6, −3.6, −4.31, −4.6; HRMS (EI) calcd for $C_{26}H_{46}O_5Si_2Se$ 574.2049, found 574.2048.

3rd fraction: **20a** (136.6 mg, 0.188 mmol, 89% with reference to starting **7b**) colorless oil; $[\alpha]$ $\Theta_{204.0\,nm} = -12800°$, $\Theta_{237.2\,nm} = +14800°$, $\Theta_{251.2\,nm} = 126°$, $\Theta_{280.6nm} = -14500°$ ($c = 0.0314$ mM in MeOH, 24 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.11$ (ddq, $J = 11.4$, 0.8, 6.4 Hz, 1H), 3.93 (ddd, $J = 8.8$, 5.4, 3.4 Hz, 1H), 3.49 (d, $J = 14.2$ Hz, 1H), 3.38 (d, $J = 14.8$ Hz, 1H), 3.07 (dd, $J = 14.0$, 3.4 Hz, 1H), 3.05–2.95 (m, 2H), 2.82 (dd, $J = 14.0$, 5.4 Hz, 1H), 2.31 (ddd, $J = 14.6$, 4.0, 0.8 Hz, 1H), 1.51 (ddd, $J = 14.6$, 11.4, 10.2 Hz, 1H), 1.35 (d, $J = 6.4$ Hz, 3H); (olivosyl) $\delta = 7.75-7.20$ (m, 5H), 5.35 (d, $J = 7.0$ Hz, 1H), 4.19 (dd, $J = 4.6$, 3.0 Hz, 1H) 3.82 (dq, $J = 2.8$, 6.8 Hz, 1H), 3.58 (dd, $J = 4.6$, 2.8 Hz, 1H), 3.18 (dd, $J = 7.0$, 3.0 Hz, 1H), 1.39 (d, $J = 6.8$ Hz, 3H), 0.97, 0.89 (2s, 18H), 0.11, 0.10, 0.07, 0.04 (4s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): (aglycon) $\delta = 199.6$, 165.3, 74.0, 69.0, 59.3, 53.3, 52.1, 46.9, 36.8, 20.6; (olivosyl) $\delta = 131.3$, 128.6, 127.0, 104.2, 101.7, 77.6, 76.2, 75.1, 50.2, 25.9, 25.8, 20.2, 18.1, −4.0, −4.2, −4.3, −4.3; HRMS (EI) calcd for $C_{34}H_{56}O_8Si_2Se$ 728.2679, found 728.2678.

5-[3,4-Bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-phenylseleno-α-D-*manno*-pyranosyloxy]-decarestrictine B (**20b**): Compound **7a** (100 mg; 0.174 mmol)was added to a solution of decarestrictine B (**4**) (41 mg, 0.19 mmol) in dry diethyl ether (10 mL) at −78 °C, which was stirred. After 15 min, TMSOTf (47 μL, 1.5 equiv) in diethyl ether (1 mL) was added and stirring was continued for 30 min at −25 °C. Workup in the usual manner and purification by flash chromatography (toluene/EtOAc 20:1) gave **20b** (117 mg, 0.16 mmol, 92%) as a colorless oil. $[\alpha]$ $\Theta_{208.0\,nm} = -14900°$, $\Theta_{232.8\,nm} = +2010°$, $\Theta_{291.6nm} = -5670°$ ($c = 0.0221$ mM in MeOH, 24 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.11$ (ddq, $J = 11.4$, 0.8, 6.4 Hz, 1H), 3.78 (ddd, $J = 9.2$, 4.8, 3.2 Hz, 1H), 3.44 (s, 2H), 3.10 (ddd, $J = 10.2$, 4.0, 4.0 Hz, 1H), 2.97 (dd, $J = 9.2$, 4.0 Hz, 1H), 2.84 (dd, $J = 14.0$, 4.8 Hz, 1H), 2.64 (br dd, $J = 14.0$, 3.2 Hz, 1H), 2.35 (ddd, $J = 14.6$, 4.0, 0.8 Hz, 1H), 1.57 (ddd, $J = 14.6$, 11.4, 10.2 Hz, 1H), 1.35 (d, $J = 6.4$ Hz, 3H); (olivosyl) $\delta = 7.64-7.20$ (m, 5H), 5.26 (d, $J = 4.8$ Hz, 1H), 4.14 (dd, $J = 5.0$, 3.4 Hz, 1H), 3.93 (dq, $J = 7.2$, 6.4 Hz, 1H), 3.66 (dd, $J = 4.8$, 3.4 Hz, 1H), 3.52 (dd, $J = 7.2$, 5.0 Hz, 1H), 1.32 (d, $J = 6.4$ Hz, 3H), 1.04, 0.92 (2s, 18H), 0.21, 0.17, 0.12, 0.12 (4s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): (aglycon) $\delta = 199.6$, 165.5, 72.3, 69.0, 58.8, 54.4, 51.9, 47.3, 36.6, 20.6; (olivosyl) $\delta = 133.2$, 130.3, 128.9, 126.9, 98.0, 76.1, 75.0, 70.7, 50.5, 26.2, 26.0, 18.8, 18.3, 18.0, −3.5, −4.2, −4.4; HRMS (EI) calcd for $C_{34}H_{56}O_8Si_2Se$ 728.2679, found 728.2678.

5-[3,4-Bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-β-D-*arabino*-pyranosyloxy]-decarestrictine B (**21a**): **20a** (30.8 mg, 0.042 mmol) was treated with triphenyltin hydride (22.3 mg, 0.064 mmol) and a catalytic amount of AIBN as described before for **16**. Flash chromatography (toluene/EtOAc 15:1) afforded **21a** (22.7 mg, 0.04 mmol, 94%) as a colorless oil. $[\alpha]$ $\Theta_{214.8\,nm} = -11600°$, $\Theta_{246.8\,nm} = -1450°$, $\Theta_{283.0\,nm} = -3490°$, $\Theta_{342.6\,nm} = -489°$, $\Theta_{441.8\,nm} = -61°$ ($c = 0.0302$ mM in MeOH, 25 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.10$ (ddq, $J = 11.7$, 0.8, 6.4 Hz, 1H), 3.89 (ddd, $J = 8.8$, 5.4, 3.6 Hz, 1H), 3.48 (d, $J = 14.4$ Hz, 1H), 3.40 (d, $J = 14.4$ Hz, 1H), 3.05 (dd, $J = 13.8$, 3.6 Hz, 1H), 3.04–2.98 (m, 2H), 2.83 (dd, $J = 13.8$, 5.4 Hz, 1H), 2.33 (ddd, $J = 14.6$, 4.0, 0.8 Hz, 1H), 1.50 (ddd, $J = 14.6$, 11.4, 10.4 Hz, 1H), 1.34 (d, $J = 6.4$ Hz, 3H); (olivosyl) $\delta = 4.81$ (dd, $J = 9.8$, 2.0 Hz, 1H), 3.63 (ddd, $J = 11.6$, 7.8, 4.8 Hz, 1H), 3.24 (dq, $J = 8.8$, 6.0 Hz, 1H), 3.15 (dd, $J = 8.8$, 7.8 Hz, 1H), 2.16 (ddd, $J = 12.6$, 4.8, 2.0 Hz, 1H), 1.61 (ddd, $J = 12.6$, 11.6, 9.8 Hz, 1H), 1.26 (d, $J = 6.0$ Hz, 3H), 0.90, 0.89 (2s, 18H), 0.09, 0.08, 0.07 (3s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): (aglycon) $\delta = 199.6$, 165.4, 72.8, 69.0, 59.5, 53.7, 52.1, 47.1, 36.8, 20.6; (olivosyl) $\delta = 98.8$, 77.8, 73.6, 73.1, 41.0, 26.3, 26.1, 18.8, 18.3, 18.0, −2.7, −3.0, −3.9, −4.1; LRMS (DCI): *m/z* (%): 590.4 (100) $[M+NH_4^+]$, 392.3 (10), 376.3 (38), 359.3 (8), 232.1 (22).

5-[3,4-Bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-α-D-*arabino*-pyranosyloxy]-decarestrictine B (**21b**): Compound **20b** (54 mg, 0.074 mmol) was treated with triphenyltin hydride (39 mg, 0.111 mmol) and a catalytic amount of AIBN as described for **16**. Flash chromatography (toluene/EtOAc 20:1) afforded **21b** (40.2 mg, 0.07 mmol, 94%) as a colorless oil. $[\alpha]$ $\Theta_{216.0\,nm} = -10600°$, $\Theta_{244.8\,nm} = -1590°$, $\Theta_{284.0\,nm} = -5910°$, $\Theta_{341.0\,nm} = -123°$, $\Theta_{472.6\,nm} = +751°$ ($c = 0.0337$ mM in MeOH, 25 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.09$ (br dq, $J = 11.4$, 6.2 Hz, 1H), 3.73 (ddd, $J = 9.0$, 4.4, 3.2 Hz, 1H), 3.42 (s, 2H), 3.08 (ddd, $J = 10.2$, 4.2, 3.8 Hz, 1H), 2.99 (dd, $J = 9.0$, 3.8 Hz, 1H), 2.94 (dd, $J = 14.0$, 4.4 Hz, 1H), 2.58 (dd, $J = 14.0$, 3.2 Hz, 1H), 2.36 (br dd, $J = 14.6$, 4.4 Hz, 1H), 1.53 (ddd, $J = 14.6$, 11.4, 10.2 Hz, 1H), 1.32 (d, $J = 6.2$ Hz, 3H); (olivosyl) $\delta = 5.11$ (br d, $J = 3.8$ Hz, 1H), 3.93 (ddd, $J = 10.8$, 8.0, 4.8 Hz, 1H), 3.85 (dq, $J = 9.0$, 6.2 Hz, 1H), 3.14 (dd, $J = 9.0$, 8.0 Hz, 1H), 2.03 (ddd, $J = 13.2$, 4.8, 1.2 Hz, 1H), 1.70 (ddd, $J = 13.2$, 11.0, 3.8 Hz, 1H), 1.17 (d, $J = 6.2$ Hz, 3H), 0.89, 0.89 (2s, 18H), 0.09, 0.07 (2s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): (aglycon) $\delta = 199.6$, 165.6, 71.4, 69.0, 58.8, 54.2, 51.9, 47.8, 36.7, 20.7; (olivosyl) $\delta = 94.8$, 78.3, 70.5, 68.8, 39.7, 26.3, 26.1, 18.5, 18.3, 18.1, −2.8, −3.1, −4.0, −4.4; LRMS (DCI): *m/z* (%): 590.4 (100) $[M+NH_4^+]$, 392.3 (7), 376.2 (40), 359.3 (8), 232.1 (11).

5-(2,6-Dideoxy-β-D-*arabino*-pyranosyloxy)-decarestrictine B (**22a**): Compound **21a** (61.2 mg, 0.107 mmol) was treated with anhydrous TBAF (112 mg, 0.428 mmol, 4 equiv) in dry THF (5 mL) for 2 h at 0 °C. Flash chromatography (silica gel, EtOAc) of the concentrated solution followed by a second chromatogaphic purification (CH_2Cl_2/MeOH 9:1) afforded **22a** (31.8 mg, 0.092 mmol, 87%) as a colorless oil. $[\alpha]$ $\Theta_{216.8\,nm} = -8950°$, $\Theta_{248.4\,nm} = -265°$, $\Theta_{286.8\,nm} = -2270°$, $\Theta_{348.2\,nm} = 135°$, $\Theta_{445.2\,nm} = -298°$ ($c = 0.0947$ mM in MeOH, 23 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.11$ (ddq, $J = 11.4$, 1.2, 6.2 Hz, 1H), 4.86 (dd, $J = 9.6$, 2.0 Hz, 1H), 3.88 (ddd, $J = 9.0$, 5.2, 3.6 Hz, 1H), 3.61 (ddd, $J = 11.6$, 8.8, 5.0 Hz, 1H), 3.48 (d, $J = 14.4$ Hz, 1H), 3.42 (d, $J = 14.4$ Hz, 1H), 3.31 (dq, $J = 9.0$, 6.0 Hz, 1H), 3.13 (dd, $J = 9.0$, 8.8 Hz, 1H), 3.04 (ddd, $J = 10.4$, 4.0, 4.0 Hz, 1H), 3.03 (dd, $J = 13.8$, 3.6 Hz, 1H), 3.01 (dd, $J = 9.0$ 4.0 Hz, 1H), 2.85 (dd, $J = 13.8$, 5.2 Hz, 1H), 2.34 (ddd, $J = 14.8$, 4.0, 1.2 Hz, 1H), 2.28 (ddd, $J = 12.4$, 5.0, 2.0 Hz, 1H), 1.65 (ddd, $J = 12.4$, 11.6, 9.6 Hz, 1H), 1.51 (ddd, $J = 14.8$, 11.4, 10.4 Hz, 1H), 1.35 (d, $J = 6.2$ Hz, 3H), 1.34 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 199.8$, 165.4, 99.1, 77.3, 74.0, 71.8, 71.6, 69.1, 59.5, 53.8, 52.1, 47.0, 39.1, 36.6, 20.6, 17.8; LRMS (DCI): *m/z* (%): 706.5 (10) $[2M+NH_4^+]$, 362.3 (100) $[M+NH_4^+]$.

5-(2,6-Dideoxy-α-D-*arabino*-pyranosyloxy)-decarestrictine B (**22b**): Compound **21b** (33.5 mg, 0.058 mmol) was treated with anhydrous TBAF (76 mg, 0.29 mmol) in dry THF (3 mL) for 12 h at RT. For the workup, the solution was purified directly by flash chromatography (EtOAc, followed by a second chromatographic purification CH_2Cl_2/MeOH 9:1) to afford the starting material **21b** (4.7 mg, 8.0 μmol) and **22b** (11.0 mg, 0.032 mmol, 55%) as a colorless oil. $[\alpha]$ $\Theta_{215.0\,nm} = -8340°$, $\Theta_{247.8\,nm} = -114°$, $\Theta_{286.4\,nm} = -4280°$, $\Theta_{342.0\,nm} = 120°$, $\Theta_{443.6\,nm} = -425°$ ($c = 0.0848$ mM in MeOH, 23 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.10$ (ddq, $J = 11.4$, 1.0, 6.2 Hz, 1H), 3.76 (ddd, $J = 9.2$, 4.6, 3.2 Hz, 1H), 3.44 (s, 2H), 3.09 (ddd, $J = 10.4$, 4.4, 4.0 Hz, 1H), 2.99 (dd, $J = 9.2$, 4.0 Hz, 1H), 2.96 (dd, $J = 14.0$, 4.6 Hz, 1H), 2.60 (dd, $J = 14.0$, 3.2 Hz, 1H), 2.45 (ddd, $J = 14.6$, 4.4, 1.0 Hz, 1H), 1.51 (ddd, $J = 14.6$, 11.4, 10.4 Hz, 1H), 1.33 (d, $J = 6.2$ Hz, 3H); (olivosyl) $\delta = 5.22$ (br d, $J = 3.6$ Hz, 1H), 3.95 (ddd, $J = 11.6$, 8.8, 5.0 Hz, 1H), 3.92 (dq, $J = 9.6$, 6.2, 1H), 3.12 (dd, $J = 9.6$, 8.8 Hz, 1H), 2.13 (ddd, $J = 13.0$, 5.0, 0.8 Hz, 1H), 2.05 (br s, 1H, exchangeable), 1.77 (ddd, $J = 13.0$, 11.5, 3.6 Hz, 1H), 1.58 (br s, 1H, exchangeable), 1.26 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): (aglycon) $\delta = 200.2$, 165.5, 70.9, 69.1, 58.7, 54.4, 51.9, 47.4, 36.6, 20.7; (olivosyl) $\delta = 94.5$, 78.1, 69.1, 67.6, 37.6, 17.6; LRMS (DCI): *m/z* (%): 706.5 (1) $[2M+NH_4^+]$, 362.3 (100) $[M+NH_4^+]$.

5-{4-*O*-[3,4-bis-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-β-D-*arabino*-pyranosyl]-2,3,6-trideoxy-α-L-*threo*-pyranosyl}-decarestrictine B (**24**): A catalytic amount of Ph_3PHBr was added to a solution of decarestrictine B (**4**) (1.8 mg, 8.3 μmol) and **10** (3.3 mg, 6.9 μmol) in dry CH_2Cl_2 (0.5 mL) at 0 °C, and the reaction mixture was stirred for 2 h. For the workup, the reaction mixture was hydrolyzed with a saturated $NaHCO_3$ solution and additional water (5 mL). After washing three times with CH_2Cl_2, the combined organic phases were dried ($MgSO_4$) and evaporated in vacuo. Flash chromatography (CH_2Cl_2/MeOH 20:1) afforded **24** (3.2 mg, 4.7 μmol, 68%) as a colorless oil. $[\alpha]$ $\Theta_{218.0\,nm} = -9290°$, $\Theta_{248.4\,nm} = -311°$, $\Theta_{286.4\,nm} = -4490°$, $\Theta_{380.0\,nm} = -160°$, $\Theta_{449.4\,nm} = 658°$, $\Theta_{489.0\,nm} = -83.7°$ ($c = 0.0313$ mM in MeOH, 24 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) $\delta = 5.10$ (ddq, $J = 11.4$, 1.0, 6.2 Hz, 1H), 3.91 (ddd, $J = 8.8$, 4.4, 3.8 Hz, 1H), 3.43 (s, 2H), 3.03–2.97 (m, 2H), 2.87 (dd, $J = 13.6$, 4.4 Hz, 1H), 2.65 (dd, $J =$

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13.6, 3.8 Hz, 1H), 2.31 (ddd, J = 14.4, 4.0, 1.0 Hz, 1H), 1.64–1.50 (m, 1H), 1.33 (d, J = 6.2 Hz, 3H); (rhodinosyl) δ = 5.21 (br d, J = 3.0 Hz, 1H), 4.08 (dq, J = 1.0, 6.4 Hz, 1H), 3.56 (m, 1H), 2.11–1.97 (m, 2H), 1.96 (m, 1H), 1.64–1.50 (m, 1H), 1.19 (d, J = 6.4 Hz, 3H); (olivosyl) δ = 4.44 (dd, J = 9.2, 1.8 Hz1H), 3.60 (ddd, J = 11.4, 7.8, 5.0 Hz, 1H), 3.18 (dq, J = 8.8, 5.8 Hz, 1H), 3.16–3.11 (m, 1H), 2.20 (ddd, J = 12.6, 5.0, 1.8 Hz, 1H), 1.67 (ddd, J = 12.6, 11.6, 9.8 Hz, 1H), 1.24 (d, J = 5.8 Hz, 3H), 0.90, 0.89 (2s, 18H), 0.10, 0.09, 0.08, 0.07 (4s, 12H); LRMS (DCI): m/z (%): 704.6 (100) [M+NH_4^+].

5-[4-*O*-(2,6-dideoxy-β-D-*arabino*-pyranosyl)-2,3,6-trideoxy-α-L-*threo*-pyranosyl]-decarestrictine B (**25**): Compound **24** (3.1 mg, 4.5 μmol) was treated with anhydrous TBAF (4.7 mg, 18 μmol) in THF (0.5 mL) at 0 °C for 2 h. For the workup, the solution was purified directly by double flash chromatography (CH_2Cl_2/MeOH 9:1) to afford **25** (1.5 mg, 3.7 μmol, 73%) as a colorless oil. [α] $\Theta_{214.0\,nm} = -5300°$, $\Theta_{244.2\,nm} = 627°$, $\Theta_{287.8\,nm} = -1880°$, $\Theta_{340.4\,nm} = 739°$, $\Theta_{445.0\,nm} = -484°$ (c = 0.0318 mM in MeOH, 24 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): (aglycon) δ = 5.10 (ddq, J = 11.4, 6.2, 1.0 Hz, 1H), 3.91 (ddd, J = 8.8, 4.4, 3.8 Hz, 1H), 3.43 (s, 2H), 3.02–2.98 (m, 2H), 2.87 (dd, J = 13.6, 4.4 Hz, 1H), 2.65 (dd, J = 13.6, 3.8 Hz, 1H), 2.31 (ddd, J = 14.8, 4.0, 1.2 Hz, 1H), 1.62–1.51 (m, 1H), 1.33 (d, J = 6.2 Hz, 3H); (rhodinosyl) δ = 5.21 (br d, J = 3.2 Hz, 1H), 4.09 (dq, J = 1.0, 6.4 Hz, 1H), 3.52 (m, 1H), 2.09–2.03 (m, 1H), 1.97–1.93 (m, 2H), 1.62–1.51 (m, 1H), 1.18 (d, J = 6.4 Hz, 3H); (olivosyl) δ = 4.52 (dd, J = 9.6, 1.9 Hz, 1H), 3.59 (ddd, J = 11.8, 8.6, 5.0 Hz, 1H), 3.26 (dq, J = 8.0, 6.0 Hz, 1H), 3.12 (dd, J = 9.0, 8.6 Hz, 1H), 2.31 (ddd, J = 12.4, 5.0, 1.9 Hz, 1H), 2.16 (br s, 1H, exchangeable), 2.03 (br s, 1H, exchangeable), 1.72 (ddd, J = 12.4, 11.8, 9.6 Hz, 1H), 1.32 (d, J = 6.0 Hz, 3H); LRMS (DCI): m/z (%): 476.5 (100) [M+NH_4^+].

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