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Synthesis of higher carbon sugars. Unexpected rearrangement of higher sugar allylic alcohols

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ABSTRACT

Coupling of a sugar phosphonate with a sugar aldehyde afforded a C_{13}-higher sugar enone. Reduction of the carbonyl function provided both stereoisomeric allylic alcohols. Inversion of the configuration at the carbinol centre in these derivatives did not yield the expected S_N2 product, but proceeded with rearrangement to the tetrahydrofuran derivative.

1. Introduction

Higher carbon sugars containing more than 10 carbon atoms in the chain are interesting synthetic targets. While the role of heptoses, octoses and nonoses in the biology of living cells is well documented and many synthetic methods have been developed to prepare these important compounds,[1] the longer analogues such as tunicamine[2] or hikozamine[3] (being components of antibiotics) are scarce in Nature. The synthesis of such demanding targets can be realized either by iterative C_1 or C_2 elongation[4] (which is a tedious and lengthy procedure) or by coupling of a sugar with a C_n unit. This fragment may be represented by an achiral unit (such as highly activated dienes, which upon reaction with sugar-derived aldehydes affords precursors of these targets[5]) or more conveniently by an already functionalized unit.

Two different classes of higher carbon sugars may be regarded. The first represents so-called C-glycosides, which possess a carbon–carbon bond at the anomeric position. Such derivatives are well known and many methods have been developed for their preparation.[6]

We are interested in another class of higher carbon sugars in which the C–C bond is created between the non-anomeric carbon atoms; especially those which are connected via terminal carbon atoms. The strategy involves reaction of properly activated sugar sub-units, which are coupled either directly or via additional C-atom(s) (Fig. 1).

One of the first examples of such methodology provided by Secrist[7] in the end of 1970s, applied the Wittig reaction for the preparation a higher sugar **3**—key-compound in the synthesis of the antibiotic sugar hikozamine. The phosphonium salt **1** derived from a properly blocked hexose was converted into an ylid **2**, which could either react with a sugar aldehyde (***R′***-CHO) affording a desired higher sugar precursor **3**, or decompose via a β-elimination process (Fig. 2).

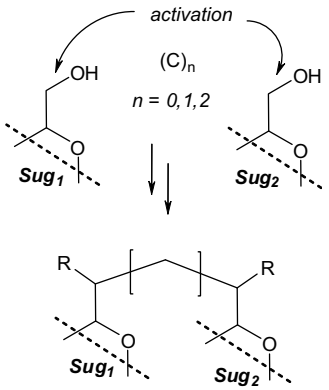

Figure 1. Synthesis of higher sugars by coupling of two properly activated sub-units.

To overcome the problem of decomposition of the phosphorane, we have introduced the stabilized Wittig reagents such as **4** and more conveniently the phosphonates **5** (Fig. 3).[8]

Both reactive intermediates were applied in the preparation of a skeleton of higher carbon sugar **6**, in which the allylic bridge flanked by two sugar sub-units is suitable for further functionalization (by stereoselective reduction of the carbonyl group and subsequent oxidation of the double bond).

In this communication, the application of our methodology for the preparation of long-chain monosaccharides, convenient precursors of complex polyhydroxylated compounds will be presented.

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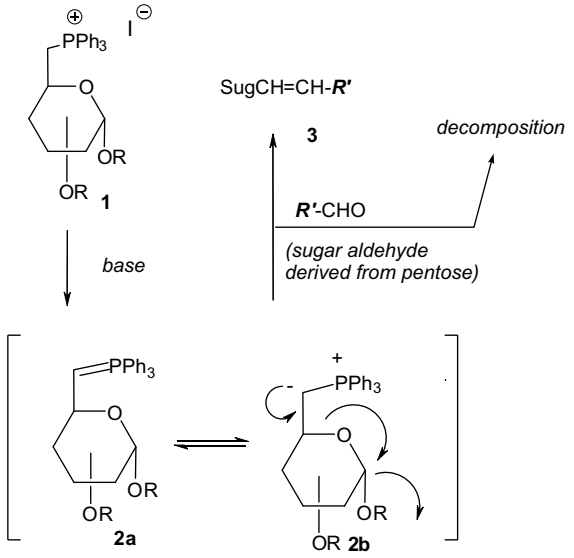


Figure 2. Synthesis of hikozamine precursor by Secrist.

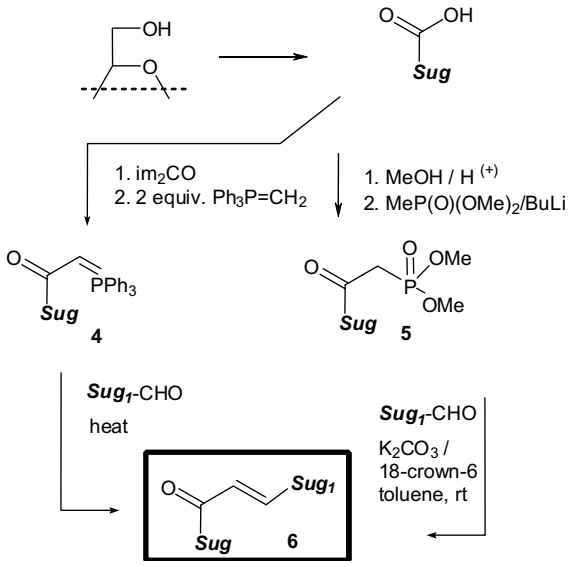


Figure 3. Synthesis of higher carbon sugars via phosphorane and phosphonate methodology.

2. Results and discussion

Recently we have prepared the higher sugar precursor **9** by reaction of the phosphonate **7** and readily available aldehyde **8** (Fig. 4).[9] Although functionalization of the allylic C6–C8 bridge could be performed highly stereoselectively and in high yield, we faced a severe problem with selective deprotection of the terminal position (C11–C12).

To overcome these difficulties in the model synthesis of long-chain monosaccharides we have designed another precursor with a readily accessible terminal position.

2.1. Synthesis of higher carbon sugars with thirteen carbon atoms in the chain

The reaction of the phoshonate **7** with the readily available 2,3,4-tri-*O*-benzyl-5,6-*O*-isopropylidene-D-glucose[10] **10** under mild

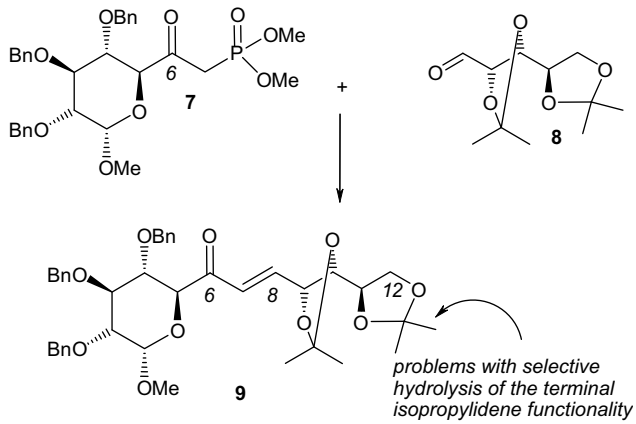
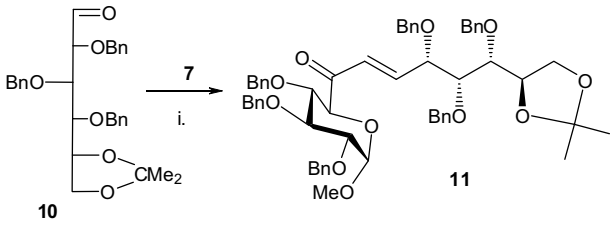


Figure 4. Synthesis of a precursor of the C_{12}-monosaccharide by phosphonate methodology.

phase transfer conditions afforded the higher sugar enone **11** in 84% yield (Scheme 1).



Scheme 1. Reagents and conditions: (i) K_2CO_3, toluene, 18-crown-6, rt, 84%.

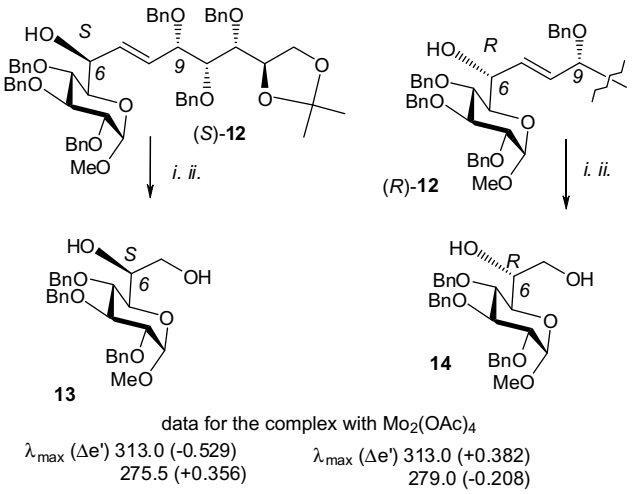
Reduction of such enones with zinc borohydride usually provides the higher sugar allylic alcohols with an (*R*)-configuration at the newly created stereogenic centre in high yield and very high stereoselectivity.[11] However, this case was an exception; treatment of the enone **11** with $Zn(BH_4)_2$ provided both alcohols (*R*)-**12** and (*S*)-**12** in almost equal amounts (Table 1). The best selectivity was observed in the reaction of the enone **11** with K-Selectride.

Table 1
Reduction of enone **12** with various agents

Reducing agent	Products **12** (*R*):(*S*)	Overall yield (%)
$Zn(BH_4)_2$	56:44	85
DIBAL-H	71:29	91
$NaBH_4$	52:48	82
K-Selectride	78:22	89
L-Selectride	76:24	80

The configuration at the newly created stereogenic centre in both alcohols was determined by CD spectroscopy, which is particularly useful for determination of the absolute configuration of the *threo*-diols.[12] Compounds (*S*)-**12** and (*R*)-**12** were converted into L-*glycero*-D-*gluco*- and D-*glycero*-D-*gluco*-heptoses, **13** and **14**, respectively (Scheme 2) by ozonolysis of the double bond, followed by reduction of the crude ozonide. The positive Cotton effect observed in the CD spectrum of the complex of diol **14** with di-molybdenum tetraacetate indicated an (*R*)-configuration at the C6-centre, while the negative value for the diastereoisomer **13** indicated a (6*S*)-configuration.

Further synthetic steps performed for both allylic alcohols provided the fully hydroxylated derivatives. First, the hydroxyl group in either alcohol was protected as a benzyl ether (**15** or **16**) and further *cis*-hydroxylated with osmium tetraoxide (catalytic version)[13] which furnished the corresponding diols: **17**/**18** (from **15**) and **19**/**20** (from **16**) (Scheme 3).



Scheme 2. Reagents: (i) O_3, CH_2Cl_2, MeOH, then Me_2S; (ii) $NaBH_4$.

The absolute configurations of all diols with the relative *threo* arrangement of both hydroxyl groups were determined by CD spectroscopy of the complexes of the diols with di-molybdenum tetraacetate. The negative Cotton effect observed for the complexes of the diols **18** and **19** with dimolybdenum tetraacetate unambiguously indicated a (7*S*,8*S*)-configuration, while the positive effect for such complexes of the diols **17** and **20** indicated a (7*R*,8*R*)-configuration at the newly created stereogenic centres (Table 2).

Table 2
Assignment of the configuration at the C7,C8 centres in diols **17**–**20** by CD

Compound	λ_{max} ($\Delta\varepsilon'$)	λ_{max} ($\Delta\varepsilon'$)	Cotton effect	Configuration
17	280 (−0.0272)	315 (+1.9978)	+	(7*R*,8*R*)
18	271.5 (+0.3274)	317.5 (−0.9066)	–	(7*S*,8*S*)
19	275.4 (+0.1171)	336.4 (−0.3706)	–	(7*S*,8*S*)
20	266.8 (−0.5628)	335.2 (+0.1961)	+	(7*R*,8*R*)

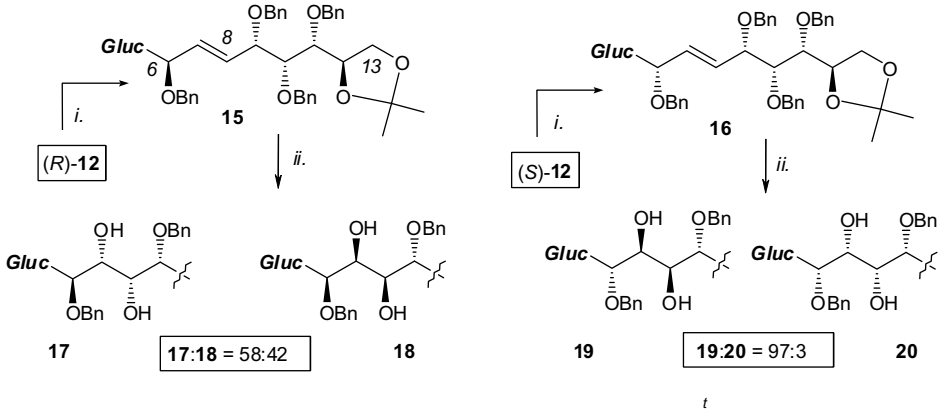
As expected from the rules elaborated upon by Kishi for the osmylation of allylic alcohols (or their derivatives),[14] the dihydroxylation of the (6*S*)-isomer **16** was highly selective and almost exclusively afforded diol **19** with an *anti*-relationship of the newly introduced hydroxyl groups to both oxygen functions flanking the double bond (ratio **19**:**20** = 97:3). Selectivity in the osmylatation of the (6*R*)-isomer **15** was low and both diols **17** and **18** were obtained in comparable amounts (**17**:**18** = 58:42).

2.2. Attempts to invert the configuration in higher sugar allylic alcohols

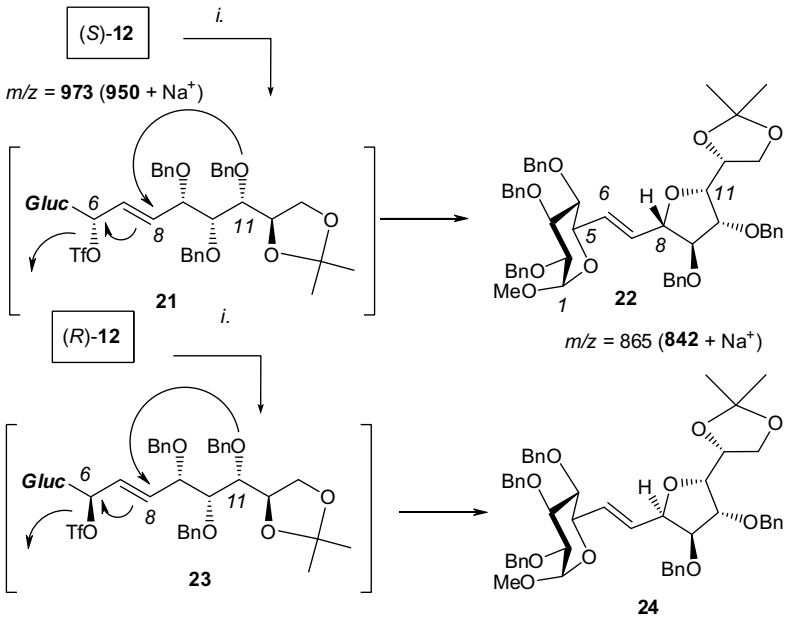
Such diols are convenient precursors of higher analogues, which can be prepared by, for example, hydrolysis of the isopropylidene grouping and further elongation at the terminal position. Since diol **19** can be obtained with very high selectivity from the corresponding allylic alcohol **16**, it should be possible to increase the overall yield of this compound by transformation of alcohol (*R*)-**12** to (*S*)-**12**. We decided, therefore, to perform a detailed study on the interconversion between these two species. The most reasonable choice for this purpose, the Mitsunobu inversion,[15] did not afford any product, and only the starting material was recovered after this reaction. We turned our attention to the classical S_N2 process, that is, activation of the hydroxyl function as a triflate followed by displacement of the leaving group with a carboxylate anion. This reaction, however, proceeded via an unexpected route. The triflate **21** [prepared from the alcohol (*S*)-**12**] underwent in situ intramolecular substitution by an oxygen from the C11 centre with simultaneous migration of the double bond towards the glucose ring (Scheme 4).

The structure of this product was assigned on the basis of the MS and NMR data. The signal in the ESI MS spectrum of the product obtained after triflation of the alcohol (*S*)-**12** observed at *m*/*z*: 865 [M+Na^+] strongly suggested the elimination of benzyl alcohol from the molecule. This was further supported by the ^{13}C NMR data in which only five signals of the quaternary carbon atoms from the benzyl groups were seen (see Section 4). Moreover in the COSY spectrum, the resonances of the double bond showed the cross peaks to H-5 and H-8, which strongly suggested that the double bond was shifted from the C7–C8 to the C6-C7 position, that is, towards the glucose ring. The *E*-configuration across the double bond was retained, as seen from the ^1H NMR spectrum in which the large coupling constant between the olefinic protons (J = 15.5 Hz) was observed. On the basis of these data, we were able to propose the cyclic structure represented by formula **22**. The only point that could not be solved by the spectroscopic data was the configuration at the newly created stereogenic centre C8. This was, however, established by X-ray crystallographic analysis; the structure of the compound **22** is shown in Figure 5.

The same process was observed when the isomeric alcohol (*R*)-**12** was triflated. The NMR spectra of this product were similar to the spectra of **22** (although it differed quite significantly) which pointed to the fact that the rearrangement of triflate **23** provided stereoisomer **24** with a different configuration at the C8 centre. The most important resonances of both cyclic products **22** and **23** are shown in Table 3.



Scheme 3. Reagents and conditions: (i) BnCl, 50% NaOH, Bu_4NBr (cat.), benzene, rt; (ii) OsO_4 (cat.), NMO, ^tBuOH, H_2O, THF, rt, 48 h.



Scheme 4. Reagents and conditions: (i) Tf_2O, CH_2Cl_2, py, 0 °C, 30 min.

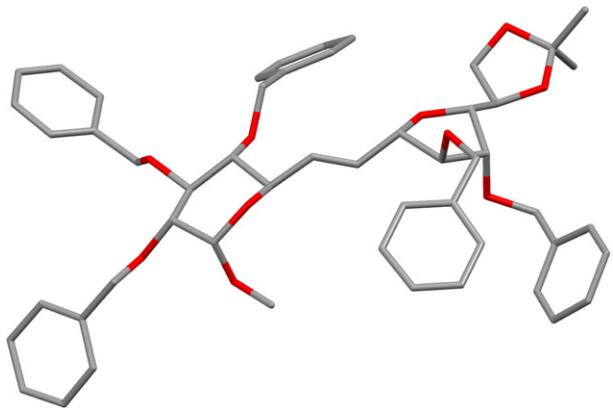


Figure 5. The X-ray structure of compound **22**.

Table 3
The NMR data for rearranged products **22** and **24**

	22 δ (ppm), J (Hz)	**24** δ (ppm), J (Hz)
H-7	5.96, dd $J_{6,7}$ = 15.5 $J_{7,8}$ = 7.5	6.0, ddd $J_{7,5}$ = 1.2 $J_{6,7}$ = 15.6 $J_{7,8}$ = 7.3
H-6	5.79, dd $J_{5,6}$ = 6.5 $J_{6,7}$ = 15.5	5.85, ddd $J_{5,6}$ = 5.8 $J_{6,7}$ = 15.6 $J_{6,8}$ = 0.8
H-8	4.32, dd $J_{7,8}$ = 7.5 $J_{8,9}$ = 3.0	4.52, dd $J_{7,8}$ = 7.3 $J_{8,9}$ = 3.6
H-9	3.8, d $J_{8,9}$ = 3.0	3.81, dd $J_{8,9}$ = 3.6 $J_{9,10}$ = 0.9
C-7	132.1	128.8
C-6	129.5	130.3
C-8	84.6	81.4
C-9	87.8	83.6

The fact that each stereoisomeric allylic alcohol was converted into a single tetrahydrofuran derivative differing from each other only by configuration at the newly created stereogenic centre at the C8 position pointed to the concerted mechanism of the rearrangement.

This process resembles similar reactions, in which the double bond is activated by iodine and then attacked by an oxygen atom bearing a benzyl group (Fig. 6).[16]

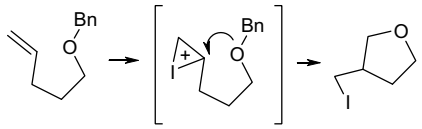


Figure 6. Cyclization of pentenyl alcohol derivatives.

However, this reaction is different; the double bond is activated by the presence of a strong electron withdrawing group (triflate) at the allylic position, so the attack of the oxygen functionality on the electron poor olefinic bond results in cyclization with *simultaneous* migration of the double bond.

3. Conclusion

The model synthesis of higher carbon sugars—tridecoses has been elaborated upon. The presence of the isopropylidene functionality at the terminal (C12–C13) position makes this 'end' readily accessible for further transformations (e.g., elongation by another sugar sub-unit which may result in even higher analogues). The unusual rearrangement of the higher sugar allylic skeleton, proceeding with the cyclization and simultaneous migration of the double bond, was observed when the allylic hydroxyl group was activated as a triflate.

4. Experimental

4.1. General

The NMR spectra were recorded in $CDCl_3$ at 303 K with a Bruker DRX Avance 500 spectrometer equipped with a TBI 50SB H-C/BB-D-

05 Z-G probehead, operating at 500.133 and 125.773 MHz for ^{1}H and ^{13}C, respectively (internal Me_4Si). The assignment of the ^{1}H and ^{13}C NMR signals was made using results of 2D methods including COSY, HSQC and DEPT correlations. The relative configurations of the protons were determined based on NOESY. The ^{1}H- and ^{13}C-aromatic resonances occurring at the typical δ values were omitted for simplicity. Mass spectra were recorded with an ESI/MS Mariner (PerSeptive Biosystem) mass spectrometer. Optical rotations were measured with a Digital Jasco polarimeter DIP-360 (λ = 589 nm) for solutions in $CHCl_3$ (c 1) at rt. CD spectra were measured between 650 and 230 nm at room temperature with a Jasco J715 spectropolarimeter using DMSO solutions in cells of 0.2 path length (spectral band width 1 nm, sensitivity 10×10^{-6} or 20×10^{-6} ΔA-unit/nm). Depending on the S/N-ratio, the λ-scan speed was 0.2 or 0.5 nm/s. For CD measurements the chiral diol (1–3 mg) was dissolved in a solution of the stock $[Mo_2(OAc)_4]$ complex (6–7 mg) in DMSO (10 mL) so that the molar ratio of the stock complex to diol was about 1:0.3 to 1:0.7. As the true concentrations of the individual optically active complexes are unknown, apparent $\Delta\varepsilon'$ values are given, calculated from the total ligand concentration and assuming 100% complexation. $[Mo_2(OAc)_4]$ and DMSO (Uvasol) were commercially available from Fluka AG and E. Merck, respectively, and were used without further purification.

Column chromatography was performed on silica gel (Merck, 70–230 or 230–400 mesh). Methylene chloride was distilled from CaH_2 and THF from potassium prior to use. Organic solutions were dried over anhydrous magnesium sulfate.

4.2. The X-ray crystallographic data of 12

Crystallographic data for the structure of **22** have been deposited with the Cambridge crystallographic Data Centre as Supplementary Publication No. CCDC 685220. Diffraction data were collected at 100 K by using a Kappa CCD diffractometer with graphite monochromated MoKα radiation. The structure was solved by direct methods (SHELXS-97) and refined on F^2 by full-matrix least-squares method (SHELXL-97). The structure contains three symmetry independent molecules of **22** all having the same absolute configuration but slightly different conformations. Formula: $3C_{52}H_{58}O_{10}$, monoclinic, space group $P2_1$, a = 23.906(1), b = 8.5731(2), c = 34.031(1) Å, β = 98.56(1)°, V = 6896.9(4) Å^3, Z = 2, $F(000)$ = 2700, μ(MoKα) = 0.08 mm^{-1}, R_1 = 0.1005 [$I > 2\sigma(I)$], wR_2 = 0.2112 for all data.

4.3. Methyl 2,3,4,9,10,11-hexa-*O*-benzyl-7,8-dideoxy-7,8-didehydro-12,13-*O*-isopropylidene-α-D-*gluco*-D-*gluco*-tridec-7(*E*)-eno-1,5-pyranosid-6-ulose 11

To a solution of aldehyde **10** (9.8 g, 20 mmol) and phosphonate **7** (14.6 g, 25 mmol) in dry toluene (500 mL) anhydrous potassium carbonate (8.5 g) was added followed by 18-crown-6 (50 mg.; Bu_4NBr can also be used as catalyst without significant decrease of the yield of the product). After stirring for 12 h at room temperature, TLC (hexane–ethyl acetate, 3:1) indicated the disappearance of the aldehyde and the formation of a new, less polar product, which was visible under UV light. Water (500 mL) was added, the organic phase was separated and the aqueous one extracted with AcOEt (500 mL). The combined organic solutions were washed with water (2 × 250 mL), brine (250 mL), dried and concentrated, and the product was isolated by column chromatography (hexane–ethyl acetate, 6:1 to 4:1) as an oil (15.9 g, 16.8 mmol, 84%).

$[\alpha]_D$ = +6.9; HR-MS m/z: 971.4341 [$C_{59}H_{64}O_{11}$ (M+Na)$^+$ requires: 971.4370]; ^{1}H NMR: δ 7.0 (dd, $J_{7,8}$ = 15.8 Hz, $J_{8,9}$ = 5.6 Hz, H-8), 6.56 (dd, $J_{7,9}$ = 1.2 Hz, H-7), 4.55 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.30–4.26 (m, 1H, H-9), 4.27 (d, $J_{4,5}$ = 9.7 Hz, H-5), 4.15–4.10 (m, 1H, H-12), 4.0 (dd, $J_{2,3} = J_{3,4}$ = 9.2 Hz, H-3), 3.93–3.84 (m, 2H, H-13′, H-13), 3.76 (dd, $J_{10,11} = J_{11,12}$ = 4.2 Hz, H-11), 3.70 (dd, H-4), 3.58 (dd, $J_{9,10}$ = 6.3 Hz, H-10), 3.42 (dd, H-2), 3.31 (s, OCH_3), 1.35 and 1.26 (2s, CMe_2); ^{13}C NMR: δ 194.6 (C-6), 144.7 (C-8), 128.2 (C-7), 138.6, 138.3, 138.1, 138.0, 137.96, 137.6 (6 × C_{quat}), 108.2 (CMe_2), 98.8 (C-1), 81.7 (C-3), 81.65 (C-10), 79.5 (C-9), 79.47 (C-2), 79.1 (C-4), 78.8 (C-11), 76.7 (C-12), 75.8, 74.9, 74.89, 74.1, 73.5 (5 × CH_2Ph), 72.9 (C-5), 72.1 (CH_2Ph), 65.9 (C-13), 55.7 (OCH_3), 26.4 and 24.9 (CMe_2).

Anal. Calcd for $C_{59}H_{64}O_{11}\cdot 1.5H_2O$: C, 72.59; H, 6,76. Found: C, 72,41; H, 6.92.

4.4. Reduction of the enone 11

To a cooled (0 °C) solution of enone **11** (9.7 g, 10.25 mmol) in dry ether (80 mL), zinc borohydride (25 mL of a 0.5 M solution in dry ether) was added and the mixture was stirred at 0 °C for 30 min. Excess of hydride was decomposed with water (25 mL), the organic phase was separated, washed with diluted (5%) sulfuric acid (50 mL), water (50 mL), dried and concentrated, and the products were isolated by column chromatography (hexane–ethyl acetate, 7:1 to 1:1) as oils. Yield of (*R*)-**12**: 4.6 g (47.6%); yield of (*S*)-**12**: 3.63 g (37.4%).

Reduction of the enone **11** with other reducing agents was performed under standard conditions and the results are presented in Table 1.

4.4.1. Alcohol (*R*)-12

$[\alpha]_D$ = +29.1; MS m/z: 973.4 [$C_{59}H_{66}O_{11}$ (M+Na)$^+$ = 973]; ^{1}H NMR: δ 5.70 (dd, $J_{6,7}$ = 6.8, $J_{7,8}$ = 15.7 Hz, H-7), 5.60 (dd, $J_{8,9}$ = 7.3 Hz, H-8), 4.55 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.33 (dd, $J_{5,6}$ = 3.7 Hz, H-6), 4.17–4.14 (m, 1H, H-12), 4.1 (dd, $J_{9,10}$ = 6.9 Hz, H-9), 4.01 (dd, $J_{2,3}$ = 9.4, $J_{3,4}$ = 9.1 Hz, H-3), 3.93 (dd, $J_{12,13'}$ = 7.2, $J_{13,13'}$ = 8.1 Hz, H-13′), 3.85 (dd, $J_{12,13}$ = 6.9 Hz, H-13), 3.83 (dd, $J_{10,11}$ = 3.9, $J_{11,12}$ = 4.1 Hz, H-11), 3.75 (dd, $J_{4,5}$ = 10.1 Hz, H-5), 3.52 (dd, H-10), 3.42 (dd, H-2), 3.39–3.35 (m, H-4), 3.33 (s, OCH_3), 1.37 and 1.26 (2s, CMe_2); ^{13}C NMR: δ 138.6, 138.59, 138.5, 138.2, 137.97, 137.92 (6 × C_{quat}), 132.6 (C-7), 130.2 (C-8), 108.0 (CMe_2), 97.7 (C-1), 82.1 (C-3), 82.1 (C-10), 80.8 (C-9), 80.1 (C-2), 79.0 (C-4), 78.9 (C-11), 76.9 (C-12), 75.5, 74.9, 74.5, 73.9, 73.2 (5 × CH_2Ph), 72.3 (C-5), 71.9 (C-6), 70.8 (CH_2Ph), 65.7 (C-13), 55.2 (OCH_3), 26.5 and 24,8 (CMe_2). Anal. Calcd for $C_{59}H_{66}O_{11}\cdot 0.5H_2O$: C, 73.80; H, 7.03. Found: C, 77.88; H, 6.79.

4.4.2. Alcohol (*S*)-12

$[\alpha]_D$ = +17.9; MS m/z: 973.4 [$C_{59}H_{66}O_{11}$ (M+Na)$^+$]; ^{1}H NMR: δ 5.68–5.65 (m, 2H, H-7, H-8), 4.50 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.30–4.28 (m, 1H, H-6), 4.15–4.10 (m, 1H, H-12), 4.11 (dd, $J_{8,9}$ = 6.3, $J_{9,10}$ = 6.4 Hz, H-9), 4.0 (dd, $J_{2,3}$ = 9.4, $J_{3,4}$ = 9.3 Hz, H-3), 3.96 (dd, $J_{12,13'}$ = 7.3, $J_{13,13'}$ = 8.1 Hz, H-13′), 3.88 (dd, $J_{12,13}$ = 6.8 Hz, H-13), 3.86 (dd, $J_{10,11}$ = 3.9, $J_{11,12}$ = 4.6 Hz, H-11), 3.66 (dd, $J_{4,5}$ = 9.6 Hz, H-4), 3.52–3.44 (m, 4H), 3.2 (s, OCH_3), 1.38 and 1.26 (2 × s, CMe_2); ^{13}C NMR: δ 138.7, 138.6, 138.5, 138.4 (double intensity), 138.3, 138.1 (6 × C_{quat}), 134.6 (C-8), 128.1 (C-7), 108.1 (CMe_2), 98.4 (C-1), 82.1 (C-3), 82.0 (C-10), 80.4 (C-9), 79.9 (C-2), 78.4 (C-11), 77.6 (C-4), 77.2 (C-12), 75.7, 75.2, 74.9, 73.8, 73.5 (5 × CH_2Ph), 72.2 (C-5), 70.8 (CH_2Ph), 69.3 (C-6), 65.7 (C-13), 55.2 (OCH_3), 26.5 and 24.9 (CMe_2). Anal. Calcd for $C_{59}H_{66}O_{11}$: C, 74.52; H, 6.95. Found: C, 74.29; H, 7.08.

4.5. Determination of the configuration of the stereogenic centres at C-6 in the allylic alcohols 12

Allylic alcohol (*S*)-**12** (123 mg, 0.129 mmol) was dissolved in methylene chloride (20 mL) containing small amounts of methanol (1 mL). The mixture was cooled to −78 °C and ozone (5% in oxygen) was bubbled through the solution until a blue colour persisted

(15 min). Dimethyl sulfide (4 equiv) was added, the mixture stirred at rt for 15 min and concentrated. The residue was dissolved in methanol (20 mL), and sodium borohydride added after which the mixture was stirred for 30 min at rt. The solution was partitioned between water (10 mL) and ether (20 mL), and the organic phase was separated, washed with water (2×10 mL), brine (10 mL), dried and concentrated. Chromatographic purification (hexane–ethyl acetate, 2:1 to 1:2) of the residue afforded the reduction product of aldehyde **10** and the heptose **13** (39 mg, 0.079 mmol, 61%). The NMR spectrum of the thus obtained compound was identical with the known heptose **13**;[17] the CD spectrum of the complex of **13** with $[Mo_2(OAc)_4]$ showed the negative Cotton effect [λ_{max} ($\Delta\varepsilon'$): 313.0 (−0.529) and 275.5 (+0.356)], which proved the 6(*S*) configuration of this molecule.

Analogously, alcohol (*R*)-**12** was converted into heptose **14**; the CD spectrum of the complex of **14** with $[Mo_2(OAc)_4]$ showed the positive Cotton effect [λ_{max} ($\Delta\varepsilon'$): 313.0 (+0.382) and 279.0 (−0.208)], which proved the (6*R*)-configuration of this molecule.

4.6. Methyl 2,3,4,6,9,10,11-hepta-*O*-benzyl-7,8-dideoxy-7,8-didehydro-12,13-*O*-isopropylidene-α-D-*glycero*-D-*gulo*-D-*gluco*-tridec-7(*E*)-eno-1,5-pyranoside 15

To a cooled (5 °C) solution of the alcohol (*R*)-**12** (159 mg; 0.167 mmol) in DMF (5 mL) containing catalytic amount (5 mg) of imidazole, sodium hydride (50% suspension in mineral oil, 28.8 mg; 1.2 equiv) was added slowly. The cooling bath was removed and the mixture was stirred for 30 min at rt. Benzyl bromide (188 mg; 1.1 equiv) was added and the stirring was continued for another 3 h at rt. The excess hydride was decomposed by the careful addition of water (1 mL), and the mixture was partitioned between ether (5 mL) and water (3 mL). The organic phase was separated and the aqueous one extracted with ether (3×5 mL). The combined organic solutions were washed with water (5 mL), brine (5 mL), dried, concentrated and the product was isolated by column chromatography (hexane–ethyl acetate, 9:1 to 4:1) to afford **15** (138.9 mg, 0.1336 mmol, 80%) as an oil. $[\alpha]_D$ = +9.3; MS *m*/*z*: 1063.5 [$C_{66}H_{72}O_{11}$ (M+Na)$^+$]. ^{1}H NMR: δ 5.78 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 15.8 Hz, H-7), 5.51 (dd, $J_{8,9}$ = 7.7 Hz, H-8), 4.64 (d, $J_{1,2}$ = 3.6 Hz, H-1), 4.17 (ddd, $J_{11,12}$ = 4.3, $J_{12,13'}$ = 7.0, $J_{12,13}$ = 6.7 Hz, H-12), 4.14–4.11 (m, 2H, H-6, H-9), 4.02 (dd, $J_{2,3}$ = 9.1, $J_{3,4}$ = 9.0 Hz, H-3), 3.96 (dd, $J_{4,5}$ = 10.3, $J_{5,6}$ = 1.5 Hz, H-5), 3.90 (dd, $J_{13,13'}$ = 8.1 Hz, H-13′), 3.87 (dd, H-13), 3.83 (dd, $J_{10,11}$ = 4.1 Hz, H-11), 3.54 (dd, $J_{9,10}$ = 6.7 Hz, H-10), 3.42 (s, O*CH*$_3$), 3.45–3.41 (m, H-2), 3.34 (dd, H-4), 1.35 and 1.26 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 138.8, 138.6, 138.5, 138.3, 138.13, 138.11, 138.06 (7 × C_{quat}), 132.4 (C-8), 131.1 (C-7), 108.2 (*C*Me$_2$), 99.6 (C-1), 82.3 (C-3), 81.2 (C-10), 80.5 (C-9), 80.2 (C-2), 79.2 (C-11), 78.2 (C-6), 78.0 (C-4), 76.6 (C-12), 75.6, 74.9, 74.5, 74.1, 73.2 (5 × CH_2Ph), 72.3 (C-5), 70.8, 70.4 (2 × CH_2Ph), 65.8 (C-13), 55.0 (OCH_3), 26.5 and 24,9 (C*Me*$_2$). Anal. Calcd for $C_{66}H_{72}O_{11}$: C, 76.15; H, 6.92. Found: C, 75.99; H, 6.91.

4.7. Methyl 2,3,4,6,9,10,11-hepta-*O*-benzyl-7,8-dideoxy-7,8-didehydro-12,13-*O*-isopropylidene-α-D-*glycero*-D-*ido*-D-*gluco*-trideca-7(*E*)-eno-1,5-pyranoside 16

This compound was prepared from (*S*)-**12** analogously as **15** in 75% yield. $[\alpha]_D$ = +44.7; MS (ESI) *m*/*z*: 1063.6 [$C_{66}H_{72}O_{11}$ (M+Na)$^+$]; ^{1}H NMR: δ 5.92 (ddd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 15.8, $J_{7,9}$ = 0.7 Hz, H-7), 5.72 (dd, $J_{8,9}$ = 7.3 Hz, H-8), 4.57 (d, $J_{1,2}$ = 3.9 Hz, H-1), 4.23–4.19 (m, 1H, H-12), 4.14–4.12 (m, 1H, H-6), 4.09–4.05 (m, 1H, H-9), 3.96 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.3 Hz, H-3), 3.93 (dd, $J_{12,13'}$ = 7.2, $J_{13,13'}$ = 8.0 Hz, H-13′), 3.85 (dd, $J_{12,13}$ = 6.8 Hz, H-13), 3.84 (dd, $J_{10,11}$ = 3.7, $J_{11,12}$ = 4.7 Hz, H-11), 3.77 (dd, $J_{4,5}$ = 9.1 Hz, H-4), 3.57 (dd, H-2), 3.48-3.44 (m, 2H, H-5, H-10), 3.09 (s, O*CH*$_3$), 1.34 and 1.25 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 138.6, 138.57, 138.51, 138.12, 138.10, 137.95, 137.6 (7 × C_{quat}), 132.0 (C-8), 131.6 (C-7), 108.2 (*C*Me$_2$), 98.2 (C-1), 82.4 (C-3), 81.8 (C-10), 79.7 (C-2), 79.6 (C-9), 78.5 (C-11), 77.4 (C-4), 76.7 (C-12), 76.4 (C-6), 75.8, 74.74, 74.71, 74.0, 73.4 (5 × CH_2Ph), 72.9 (C-5), 70.8, 70.7 (2 × CH_2Ph), 65.7 (C-13), 55.0 (OCH_3), 26.4 and 24.9 (C*Me*$_2$). Anal. Calcd for $C_{66}H_{72}O_{11}$ + 1/2 H_2O: C, 75.50; H, 6.96. Found: C, 75.39; H, 7.07.

4.8. Osmylation of compound 15

To a solution of olefin **15** (0.1092 g, 0.105 mmol) in THF (8 mL) containing *tert*-butyl alcohol (0.8 mL) and water (0.1 mL), *N*-methylmorpholine-*N*-oxide (160 mg, 1.2 mmol) and osmium tetraoxide (0.5 mL of a ∼2% solution in ^{t}BuOH) were added and the mixture was stirred at room temperature (TLC monitoring in hexane–ethyl acetate, 3:1) for 48 h. Methanol (20 mL) was added followed by saturated aq $NaHSO_3$, the mixture was stirred for 30 min, then filtered through Celite and the solution was partitioned between water (20 mL) and AcOEt (100 mL). The organic phase was separated, washed with water (2 × 50 mL), brine (50 mL), dried, concentrated and the products were isolated by column chromatography (hexane–ethyl acetate, 3:1 to 2:1) as an inseparable (58:42) mixture of methyl 2,3,4,6,9,10,11-hepta-*O*-benzyl-12,13-*O*-isopropylidene-α-D-*arabino*-D-*gulo*-D-*gluco*-**17** and α-D-*arabino*-D-*gluco*-D-*gluco*-trideca-1,5-pyranoside **18** (100 mg, 0.09 mmol, 86%). Separation of these diols was possible [after their conversion into di-benzoates (with 2.2 equiv BzCl in pyridine containing DMAP)] by preparative TLC (hexane–ethyl acetate, 6:1).

4.8.1. Dibenzoate 17-Bz

$[\alpha]_D$ = −3.0; MS *m*/*z*: 1305.5 [$C_{80}H_{82}O_{15}$ (M+Na)$^+$]; ^{1}H NMR δ (MeOD): 6.44 (dd, $J_{7,8}$ = 1.7, $J_{8,9}$ = 8.0 Hz, H-8), 5.95 (dd, $J_{6,7}$ = 7.7 Hz, H-7), 4.70 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.15 (dd, J = 6.9, J = 11.2 Hz, H-12), 4.08 (d, H-6), 4.02 (dd, $J_{9,10}$ = 3.6 Hz, H-9), 3.94–3.90 (m, 2H, H-13′, H-5), 3.81 (dd, $J_{10,11}$ = 7.2 Hz, H-10), 3.80–3.75 (m, 3H, H-3, H-13, H-11), 3.64 (dd, $J_{3,4}$ = 8.7, $J_{4,5}$ = 10.4 Hz, H-4), 3.14 (dd, $J_{2,3}$ = 9.6 Hz, H-2), 3.24 (s, O*CH*$_3$), 1.2 and 1.06 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 167.1 and 166.9 (2 × C═O), 140.0, 139.9, 139.6, 139.5, 139.4, 139.2, 138.7, 138.1, 137.4 (9 × C_{quat}), 134.9 and 134.5 (2 × C-*orto*), 109.1 (*C*Me$_2$), 99.3 (C-1), 83.5 (C-3), 87.1 (C-2), 81.6 (C-9), 81.4 (C-10), 80.2, 80.15, 79.3 (C-4), 78.6 (C-12), 76.3, 76.2 (double intensity), 75.9, 75.6, 75.0, 74.1 (7 × CH_2Ph), 73.0 (C-8), 72.2 (C-7), 72.0 (C-5), 66.5 (C-13), 56.4 (OCH_3), 26.8 and 25.0 (C*Me*$_2$).

4.8.2. Dibenzoate 18-Bz

$[\alpha]_D$ = +37.4; MS *m*/*z*: 1305.5 [$C_{80}H_{82}O_{15}$ (M+Na)$^+$]; ^{1}H NMR: δ 6.27 (dd, $J_{7,8}$ = 1.3, $J_{6,7}$ = 8.8 Hz, H-7), 5.82 (dd, $J_{8,9}$ = 4.1 Hz, H-8), 4.67 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.21 (d, $J_{4,5}$ = 9.99 Hz, H-5), 4.15 (dd, $J_{9,10}$ = 7.6 Hz, H-9), 4.03–3.97 (m, 4H, H-3, H-6, H-11, H-12), 3.83 (dd, $J_{12,13'}$ = 7.0, $J_{13,13'}$ = 8.2 Hz, H-13′), 3.81 (dd, $J_{3,4}$ = 9.2 Hz, H-4), 3.72 (dd, $J_{10,11}$ = 3.5 Hz, H-10), 3.66 (dd, $J_{12,13}$ = 6.9 Hz, H-13), 3.51 (dd, $J_{2,3}$ = 9.7 Hz, H-2), 3.36 (s, OCH_3), 1.31 and 1.19 (2 × s, CMe_2); ^{13}C NMR: δ 167.1 and 166.9 (2 × C═O), 140.1, 139.8, 139.76, 139.7, 139.5, 139.2, 139.1, 137.8, 134.8 (9 × C_{quat}), 134.1 and 132.0 (2 × C-*ortho*), 109.9 (*C*Me$_2$), 98.6 (C-1), 83.3 (C-3), 81.43 (C-2), 81.41 (C-10), 81.0 (C-11), 79.7 (C-4), 79.0 (C-9), 78.5 (C-6), 77.7 (C-12), 76.2, 76.0. 75.97, 75.6, 75.4, 74.1, 73.9 (7 × CH_2Ph), 73.3 (C-8), 72.6 (C-7), 71.7 (C-5), 67.2 (C-13), 55.5 (O*CH*$_3$), 26.7 and 25.4 (C*Me*$_2$).

4.9. Osmylation of the olefin 16

Osmylation of olefin **16** (performed analogously as for **15**) provided two products which were separated by column chromato-

graphy (hexane–ethyl acetate, 5:1 to 3:1); diol **19** (81%) and **20** (2.4%).

4.9.1. Methyl 2,3,4,6,9,10,11-hepta-*O*-benzyl-12,13-*O*-isopropylidene-α-D-*arabino*-D-*ido*-D-*gluco*-trideca-1,5-pyranoside 19

$[\alpha]_D$ = +11.1; MS *m*/*z*: 1097.5 [$C_{66}H_{74}O_{13}$ (M+Na)$^+$]; ^{1}H NMR: δ 4.64 (d, $J_{1,2}$ = 3.6 Hz, H-1), 3.57 (dd, $J_{2,3}$ = 9.7 Hz, H-2), 4.14–4.03 (m, 4H, H-3, H-5, H-8), 3.92–3.84 (m, 3H, H-13′, H-13, H-9), 3.68 (dd, $J_{9,10}$ = 4.7, $J_{10,11}$ = 8.8 Hz, H-10), 3.70 (dd, $J_{3,4}$ = 9.7 $J_{4,5}$ = 9.8 Hz, H-4), 4.25–4.20 (m, H-12), 4.0 (dd, $J_{11,12}$ = $J_{10,11}$ = 8.5 Hz, H-11), 3.36 (s, O*CH*$_3$), 1.36 and 1.25 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 138.7, 138.6, 138.2, 138.18, 138.1, 137.7, 137.5 (7 × C_{quat}), 108.3 (*C*Me$_2$), 98.0 (C-1), 82.6, 80.1 (C-2), 80.07 (C-10), 78.2 (C-11), 77.2 (C-12), 76.9 (C-4), 76.7, 76.5 (C-9), 75.6, 74.4, 74.1, 74.0, 73.9, 73.7, 73.3 (7 × CH_2Ph), 70.0, 69.4, 68.7, 65.7 (C-13), 55.3 (O*CH*$_3$), 26.4 and 25.1 (C*Me*$_2$). Anal. Calcd for $C_{66}H_{74}O_{13}$: C, 73.74; H, 6.89. Found: C, 73.76; H, 6.97.

4.9.2. Methyl 2,3,4,6,9,10,11-hepta-*O*-benzyl-12,13-*O*-isopropylidene-α-D-*arabino*-D-manno-D-*gluco*-trideca-1,5-pyranoside 20

MS *m*/*z*: 1097.5 [$C_{66}H_{74}O_{13}$ (M+Na)$^+$]; ^{1}H NMR: δ 4.63 (d, $J_{1,2}$ = 3.3 Hz, H-1), 4.45 (dd, 1H, *J* = 8.8, *J* = 11.5 Hz), 4.22 (m, 1H), 4.13–4.03 (m, 4H), 3.97 (t, 1H, *J* = 4.3 Hz), 3.92–3.83 (m, 3H), 3.60 (m, 1H), 3.56 (dd, $J_{2,3}$ = 9.7 Hz, H-2), 3.36 (s, O*CH*$_3$), 1.35 and 1.25 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 138.7, 138.6, 138.2, 138.22, 138.1, 137.7, 137.5 (7 × C_{quat}), 108.3 (*C*Me$_2$), 97.9 (C-1), 82.6, 80.2, 80.1, 78.3, 76.5, 75.6, 74.4, 74.1, 74.0, 73.99, 73.8, 73.3 (7 × CH_2Ph), 70.0, 69.4, 68.8, 70.0, 69.4, 68.8, 65.7 (C-13), 55.3 (O*CH*$_3$), 26.4 and 25.1 (C*Me*$_2$).

4.10. Methyl 8,11-anhydro-2,3,4,9,10-penta-*O*-benzyl-6,7-dideoxy-6,7-didehydro-12,13-*O*-isopropylidene-α-D-*glycero*-D-*gulo*-D-*gluco*-tridec-6(*E*)-eno-1,5-pyranoside 22

This reaction was performed under an argon atmosphere. A solution of allyl alcohol (*S*)-**12** (119.7 mg, 0.126 mmol) in dry CH_2Cl_2 (5 mL), containing dry pyridine (0.25 mL) was cooled to 0 °C, and triflic anhydride (53.2 g, 0.189 mmol, 1.5 equiv) was added in one portion. After stirring for 30 min at 0 °C (TLC monitoring in hexane–ethyl acetate, 2:1), the mixture was partitioned between CH_2Cl_2 (5 mL) and water (3 mL). The organic phase was separated, washed with 10% CH_3COONa (3 × 3 mL), dried, concentrated, and the product was isolated by column chromatography (hexane–ethyl acetate, 2:1). It was further crystallized from methanol to afford pure **22** (79.6 mg, 0.0945 mmol, 75%); mp: 100–101 °C; $[\alpha]_D$ = −4.7; MS *m*/*z*: 865.4 [$C_{59}H_{66}O_{11}$ (M+Na)$^+$]; ^{1}H NMR: δ 5.96 (dd, $J_{6,7}$ = 15.5, $J_{7,8}$ = 7.5 Hz, H-7), 5.79 (dd, $J_{5,6}$ = 6.5 Hz, H-6), 4.57 (d, $J_{1,2}$ = 3.3 Hz, H-1), 4.41–4.35 (m, 1H, H-12), 4.32 (dd, $J_{8,9}$ = 3.0 Hz, H-8), 4.1 (dd, $J_{4,5}$ = 9.4 Hz, H-5), 4.05–3.93 (m, 5H, H-3, H-13′, H-13, H-10, H-11), 3.81 (d, H-9), 3.51 (dd, $J_{2,3}$ = 9.7 Hz, H-2), 3.35 (s, O*CH*$_3$), 3.25 (dd, $J_{3,4}$ = 9.5 Hz, H-4), 1.39 and 1.36 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 138.8, 138.2, 138.1, 138.0, 137.6 (5 × C_{quat}), 132.1 (C-7), 129.5 (C-6), 108.8 (*C*Me$_2$), 98.1 (C-1), 87.8 (C-9), 84.6 (C-8), 82.6 (C-10), 82.2 (C-4), 82.17 (C-11), 81.6 (C-3), 79.8 (C-2), 75.8, 75.0, 73.3 (3 × CH_2Ph), 73.0 (C-12), 71.9, 71.7 (2 × CH_2Ph), 70.5 (C-5), 67.4 (C-13), 55.2 (O*CH*$_3$), 26.7 and 25.5 (C*Me*$_2$). Anal. Calcd for $C_{59}H_{66}O_{11}$ + H_2O: C, 73.14; H, 7.02. Found: C, 73.21; H, 6.99. The X-ray structure is presented in Figure 5.

4.11. Methyl 8,11-anhydro-2,3,4,9,10-penta-*O*-benzyl-6,7-dideoxy-6,7-didehydro-12,13-*O*-isopropylidene-α-D-*glycero*-D-*ido*-D-*gluco*-tridec-6(*E*)-eno-1,5-pyranoside 24

This compound was prepared analogously as **22** from alcohol (*R*)-**12** in 75% yield. MS *m*/*z*: 865.4 [$C_{59}H_{66}O_{11}$ (M+Na)$^+$]; ^{1}H NMR: δ 6.0 (ddd, $J_{5,7}$ = 1.2, $J_{6,7}$ = 15.6, $J_{7,8}$ = 7.3 Hz, H-7), 5.85 (ddd, $J_{6,7}$ = 5.8, $J_{6,8}$ = 0.8 Hz, H-6), 4.58 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.52 (dd, $J_{8,9}$ = 3.6 Hz, H-8), 4.33 (ddd, $J_{11,12}$ = 8.0, $J_{12,13}$ = 6.2, $J_{12,13'}$ = 6.2 Hz, H-12), 4.14 (dd, $J_{10,11}$ = 3.6 Hz, H-11), 4.11 (d, H-5), 4.10 (dd, $J_{13,13'}$ = 8.5 Hz, H-13′), 4.04 (dd, $J_{9,10}$ = 0.9 Hz, H-10), 3.97 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.2 Hz, H-3), 3.95 (dd, H-13), 3.81 (dd, H-9), 3.51 (dd, H-2), 3.33 (s, O*CH*$_3$), 3.25 (dd, $J_{4,5}$ = 9.6 Hz, H-4),1.39 and 1.36 (2 × s, C*Me*$_2$); ^{13}C NMR: δ 138.8, 138.3, 138.2, 138.0, 137.9 (5 × C_{quat}), 130.3 (C-6), 128.8 (C-7), 108.8 (*C*Me$_2$), 98.1 (C-1), 83.6 (C-9), 82.4 (C-4), 81.8 (C-10), 81.76 (C-3), 81.4 (C-11), 81.37 (C-8), 80.0 (C-2), 75.8, 75.0, 73.4 (3 × CH_2Ph), 73.2 (C-12), 72.6, 72.1 (2 × CH_2Ph), 70.1 (C-5), 69.3 (C-6), 67.6 (C-13), 55.1 (O*CH*$_3$), 26.8 and 25.6 (C*Me*$_2$).

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