New strategy to sugar dienes, useful building blocks for the synthesis of bicyclic derivatives

Grzegorz Witkowski and Sławomir Jarosz*

Institute of Organic Chemistry,
Polish Academy of Sciences,
Kasprzaka 44, 01-224 Warszawa

Supporting Information, part 1

Experimental procedures

* Corresponding author:
Fax: (+48-22) 632-66-81
E-mail: slawomir.jarosz@icho.edu.pl
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General Informations

NMR spectra were recorded in CDCl₃ (internal Me₄Si) with a Varian AM-600 (600 MHz ¹H, 150 MHz ¹³C) at room temperature. Chemical shifts (δ) are reported in ppm relative to Me₄Si (δ 0.00) for ¹H and residual chloroform (δ 77.00) for ¹³C. All significant resonances (carbon skeleton) were assigned by COSY (¹H-¹H), HSQC (¹H-¹³C), and HMBC (¹H-¹³C) correlations. Reagents were purchased from Sigma-Aldrich, Alfa Aesar or ABCR, and used without further purification. Commercial: THF, CH₂Cl₂ and MeOH were dried over freshly activated (for at least 24h at 250˚C) 3Å molecular sieves for at least three days. Hexanes (65-80˚C fraction from petroleum) and EtOAc were purified by distillation. Other solvents were used without further purification. Thin-layer chromatography was carried out on silica gel 60 F₂₅₄ (Merck). Flash chromatography was performed on Büchi glass columns packed with silica gel 60 (400-600 mesh, Merck), using Knauer Smartline system with a Büchi fraction collector. HPLC analyses were performed on a Merck chromatograph equipped with the UV Detector and Merck LiChrospher® 100 RP-18 column (250×0.4 mm, 5 μm). The organic solutions were dried over MgSO₄.

** tert-Butyldiphenylsilyl 2,3,4-tri-O-benzyl-β-D-glucopyranoside (16).**

** Silvylation:** 6-O-acetyl-2,3,4-tri-O-benzyl-β-D-glucopyranose (15, 3.21 g, 6.52 mmol) and imidazole (0.89 g, 13.04 mmol) were dissolved in dry CH₂Cl₂ (65 mL). tert-Butyl(chloro)diphenylsilane (1.84 ml, 7.17 mmol) was added within 1h via a syringe pump. After additional 1h TLC (3:1 hexanes-EtOAc) indicated disappearance of the starting material (Rf 0.1) and formation of a new product (Rf 0.7). The solution was filtered through a short pad of silica, washed with 1M sulfuric acid (30 mL), dried, and concentrated under reduced pressure. Small sample (50 mg) was purified by flash chromatography (1:15→1:13→1:11→1:9 hexanes-EtOAc) to afford tert-butyldiphenylsilyl 6-O-acetyl-2,3,4-tri-O-benzyl-β-D-glucopyranoside as a colorless oil.

[a]⁺²¹_D = −38.9 (c 0.50, CHCl₃);

¹H NMR δ 7.45–7.15 (m, 25H, arom.), 5.04 (d, J = 11.0 Hz, 1H, OCH₂Ph), 4.91 (d, J = 10.9 Hz, 1H, OCH₃Ph), 4.82 (m, 2H, OCH₂Ph), 4.76 (d, J = 10.9 Hz, 1H), 4.62 (d, J = 7.3 Hz, 1H, H-1), 4.52 (d, J = 11.0 Hz, 1H, OCH₃Ph), 4.05 (dd, J = 11.7, 2.2 Hz, 1H, H-6), 3.98 (dd, J = 11.7, 5.3 Hz, 1H, H-6’), 3.55 (m, 2H, H-2 and H-3), 3.49 (dd, J = 9.8, 8.6 Hz, 1H, H-4), 3.16 (ddd, J = 9.8, 5.3, 2.2 Hz, 1H, H-5), 1.90 (s, 3H, OAc), 1.11 (s, 9H, OSiPh₂C(CH₃)₃);
$^{13}$C NMR δ 170.6 (COOCH$_3$), 138.4, 138.3 and 137.8 (quat. benzyl), 136.0–127.2 (arom.), 97.8 (C-1), 84.8 (C-3), 83.9 (C-2), 77.7 (C-4), 75.6 (OCH$_3$Ph), 75.0 (OCH$_2$Ph), 74.8 (OCH$_2$Ph), 72.5 (C-5), 63.0 (C-6), 26.9 (OSiPh$_2$C(CH$_3$)$_3$), 20.8 (COOCH$_3$), 19.2 (OSiPh$_2$C(CH$_3$)$_3$);

HRMS: m/z calcld for C$_{45}$H$_{50}$O$_7$NaSi [M+Na]$^+$: 753.3224; found: 753.3202;

elem. anal.: calcld for C$_{45}$H$_{50}$O$_7$Si: %C 74.97, %H 7.02; found: %C 74.96, %H 7.27.

**Deacylation:** Crude tert-butyldiphenylsilyl 6-O-acetyl-2,3,4-tri-O-benzyl-$\beta$-D-glucopyranoside from the above preparation was dissolved in dry MeOH (65 mL). Freshly prepared solution of MeONa in MeOH (0.5 M, 13 mL) was added and after 15 min TLC (5:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.5) and formation of a new product ($R_f$ 0.4). Solution was filtered through a short pad of silica and concentrated. Residue was dissolved in Et$_2$O (130 mL) and again filtered through a short pad of silica and concentrated. The crude product was purified by flash chromatography (1:13→1:11→1:9→1:7 hexanes-EtOAc) to afford **16** (3.41 g, 76%) as a colorless oil.

[$\alpha$]$^2$$^\circ_D$ = 32.1 (c 0.50, CHCl$_3$);

$^1$H NMR δ 7.73–7.69 (m, 5H, arom.), 7.44–7.19 (m, 20H, arom.), 5.12 (d, J = 10.9 Hz, 1H, OCH$_2$Ph), 4.91 (d, J = 10.9 Hz, 1H, OCH$_2$Ph), 4.86 (d, J = 10.9 Hz, 1H, OCH$_2$Ph), 4.77 (m, 2H, OCH$_2$Ph), 4.76 (d, J = 7.5 Hz, 1H, H-1), 4.53 (d, J = 11.1 Hz, 1H, OCH$_2$Ph), 3.58 (t, J = 9.1 Hz, 1H, H-3), 3.52 (dd, J = 9.1, 7.5 Hz, 1H, H-2), 3.45–3.40 (m, 2H, H-4 and H-6), 3.33 (ddd, J = 11.8, 6.8, 5.4 Hz, 1H, H-6'), 2.97 (ddd, J = 9.6, 5.4, 2.7 Hz, 1H, H-5), 1.11 (s, 9H, OSiPh$_2$C(CH$_3$)$_3$), 1.03 (t, J = 6.8 Hz, 1H, OH);

$^{13}$C NMR δ 138.5, 138.4 and 138.0 (quat. benzyl), 135.7–127.5 (arom.), 98.1 (C-1), 84.6 (C-3), 84.2 (C-2), 77.8 (C-4), 75.7 (OCH$_2$Ph), 75.1 (OCH$_2$Ph), 75.0 (C-5), 74.9 (OCH$_2$Ph), 61.9 (C-6), 26.9 (OSiPh$_2$C(CH$_3$)$_3$), 19.1 (OSiPh$_2$C(CH$_3$)$_3$);

HRMS: calcld for C$_{43}$H$_{48}$O$_6$NaSi [M+Na]$^+$: 711.3118; found: 711.3091;

elem. anal.: calcld for C$_{43}$H$_{48}$O$_6$Si: %C 73.94, %H 6.89; found: %C 73.91, %H 6.98.

Methyl 2,3,4-tri-O-benzyl -7-(trimethylsilyl)-7,8,9-trideoxy-$\alpha$-D-gluco-nona-8-enopyranoside.

![Methyl 2,3,4-tri-O-benzyl -7-(trimethylsilyl)-7,8,9-trideoxy-$\alpha$-D-gluco-nona-8-enopyranoside](image)

**Oxidation:** Methyl 2,3,4-tri-O-benzyl-$\alpha$-D-glucopyranoside (**8**, 3.12 g, 6.72 mmol) and TEMPO (10.5 mg, 67.2 µmol) were dissolved in dry CH$_2$Cl$_2$ (75 mL) and placed in a water/ice bath.
Trichloroisocyanuric acid (1.64 g, 7.06 mmol) was added in one portion and after 15 min TLC (7:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.4) and formation of a new product ($R_f$ 0.3). Mixture was filtered through a Celite pad, diluted with Et$_2$O (75 mL), washed with 5% Na$_2$S$_2$O$_3$ (10 mL), 1 M NaOH (25 mL), 1 M sulfuric acid (25 mL), water (25 mL) and brine (25 mL), dried, and concentrated. The residue was dissolved in toluene (50 mL) and evaporated to afford crude aldehyde.

**Allylboration:** This crude aldehyde was dissolved in dry toluene (70 mL) to which pinacol (E)-1-(trimethylsilyl)-1-propene-3-boronate (1.61 g, 6.72 mmol) was added and the mixture was stirred for 3 weeks after which TLC (5:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.1) and formation of two new products ($R_f$ 0.6 and 0.7). Solution was passed through a column of silica and evaporated to afford crude silanol as a mixture of (anticipated) anti diastereomers.

**Nozaki–Hiyama coupling:** Double-neck flask was immersed in iPrOH/solid CO$_2$ bath. Tablets of LiAlH$_4$ (0.51 g, 13.4 mmol) and anhydrous CrCl$_3$ (4.26 g, 26.9 mmol) were added and air was replaced with argon by three cycles vacuum/argon. Dry THF (75 mL) was slowly transferred via canulla and cooling bath was removed. The suspension was vigorously stirred for 1 h at rt; at this point suspension changed color from violet to black. Mixture was placed again in iPrOH/solid CO$_2$ bath and a solution of the crude aldehyde 8 (obtained in the previous step) in dry THF (10 mL) was added followed by addition of a solution of 1-bromo-1-(trimethylsilyl)-prop-2-ene (2.60 g, 13.4 mmol) in dry THF (10 mL) within 30 min via a syringe pump. Cooling bath was removed and the suspension was stirred overnight. TLC (5:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.1) and formation of two new products ($R_f$ 0.6 and 0.7). The product of the reduction of aldehyde with LiAlH$_4$ ($R_f$ 0.2) was also observed. Water (25 mL) was added and a solution was saturated with solid NaCl. Phases were separated and organic one was dried, and concentrated to afford crude silanol as mixture of anti (anticipated) diastereomers.

**Methyl 2,3,4-tri-O-benzyl-6,7,8,9-tetradecoxy-α-D-gluco-nonadi-6(E),8-enopyranoside (10).**

Crude silanol was dissolved in THF (70 mL) to which concentrated sulfuric acid (7.2 mL, 134 mmol) was added within 5 min. After 10 min TLC (7:1 hexanes-EtOAc) indicated disappearance of
the starting material ($R_f$ 0.5 and 0.6) and formation of a new product ($R_f$ 0.7). Ether (140 mL) and water (70 mL) were added and the solution was saturated with NaCl. Phases were separated and the organic one was dried, and concentrated. The residue was purified by flash chromatography (11:1→9:1→7:1→5:1 hexanes-Et$_2$O) to afford 11 (2.32 g, 71% yield from 8) as a white amorphous solid.

$[\alpha]^20_D = 7.1$ (c 0.50, CHCl$_3$);

$^1$H NMR $\delta$ 7.38–7.23 (m, 15H, arom.), 6.39–6.27 (m, 2H, H-7 and H-8), 5.66 (dd, $J = 14.4$, 6.9 Hz, 1H, H-6), 5.24 (dd, $J = 16.2$, 1.2 Hz, 1H, H-9’), 5.13 (dd, $J = 9.4$, 1.7 Hz, 1H, H-9), 4.95 (d, $J = 10.8$ Hz, 1H, OCH$_2$Ph), 4.84 (d, $J = 10.8$ Hz, 1H, OCH$_3$Ph), 4.80 (d, $J = 12.1$ Hz, 1H, OCH$_2$Ph), 4.76 (d, $J = 10.7$ Hz, 1H, OCH$_2$Ph), 4.67 (d, $J = 12.1$ Hz, 1H, OCH$_2$Ph), 4.59 (d, $J = 3.5$ Hz, 1H, H-1), 4.57 (d, $J = 10.7$ Hz, 1H, OCH$_2$Ph), 4.12 (dd, $J = 9.7$, 7.1 Hz, 1H, H-5), 3.98 (t, $J = 9.3$ Hz, 1H, H-3), 3.52 (dd, $J = 9.7$, 3.6 Hz, 1H, H-2), 3.37 (s, 3H, OCH$_3$), 3.24 (t, $J = 9.3$ Hz, 1H, H-4);

$^{13}$C NMR $\delta$ 138.8, 138.2 and 138.0 (quat. benzyl), 136.3 (C-7), 133.9 (C-8), 130.3 (C-6), 128.4–127.6 (arom.), 118.2 (C-9), 98.1 (C-1), 82.2 (C-4), 81.7 (C-3), 79.8 (C-2), 75.9 (OCH$_2$Ph), 75.2 (OCH$_2$Ph), 73.4 (OCH$_2$Ph), 70.9 (C-5), 55.20 (OCH$_3$);

HRMS: calcd for C$_{31}$H$_{34}$O$_5$Na [M+Na]$^+$: 509.2299; found: 509.2307;

elem. anal.: calcd for C$_{31}$H$_{34}$O$_5$: %C 76.52, %H 7.04; found: %C 76.66, %H 6.96.

**Methyl 2,3,4-tri-O-benzyl-6,7,8,9-tetradeoxy-α-D-gluco-nonadi-6(Z),8-enopyranoside (11).**

Crude silanol was dissolved in THF (70 mL) to which KH (30% dispersion in mineral oil, 1.80 g, 13.4 mmol) was added within 5 min. After 5 min TLC (7:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.5 and 0.6) and formation of a new product ($R_f$ 0.7). Ether (140 mL) and water (70 mL) were added and solution was saturated with NaCl. Phases were separated and the organic one was dried, concentrated, and the residue was purified by flash chromatography (11:1→9:1→7:1→5:1 hexanes-Et$_2$O) to afford 11 (2.48 g, 76% yield from 8) as a white amorphous solid.

$[\alpha]^20_D = -69.0$ (CHCl$_3$);

$^1$H NMR $\delta$ 7.37–7.22 (m, 15H, arom.), 6.75 (dt, $J = 16.8$, 10.6 Hz, 1H, H-8), 6.25 (t, $J = 11.0$ Hz, 1H, H-7), 5.39 (t, $J = 9.9$ Hz, 1H, H-6), 5.31 (dd, $J = 16.8$, 1.7 Hz, 1H, H-9’), 5.21 (d, $J = 10.1$ Hz,
1H, H-9), 4.94 (d, J = 10.8 Hz, 1H, OCH$_2$Ph), 4.82 (d, J = 10.5 Hz, 1H, OCH$_2$Ph), 4.80 (d, J = 11.7 Hz, 1H, OCH$_2$Ph), 4.69 (d, J = 10.5 Hz, 1H, OCH$_2$Ph), 4.67 (d, J = 12.1 Hz, 2H, OCH$_2$Ph), 4.61 (d, J = 10.6 Hz, 1H, OCH$_2$Ph), 4.58 (d, J = 10.3 Hz, 1H, H-1), 4.56 (d, J = 3.7 Hz, 1H, H-5), 4.00 (t, J = 9.3 Hz, 1H, H-3), 3.53 (dd, J = 9.7, 3.5 Hz, 1H, H-2), 3.40 (s, 3H, OCH$_3$), 3.30 (t, J = 9.3 Hz, 1H, H-4);

$^{13}$C NMR δ 138.8, 138.2 and 138.0 (quat. benzyl), 134.1 (C-7), 132.3 (C-8), 128.4–127.6 (arom.), 120.0 (C-9), 98.3 (C-1), 82.4 (C-4), 81.5 (C-3), 79.7 (C-2), 75.9, 75.2 and 73.4 (OCH$_2$Ph), 66.6 (C-5), 55.4 (OCH$_3$);

HRMS: calcd for C$_{31}$H$_{34}$O$_5$Na [M+Na]$^+$: 509.2299; found: 509.2309;

elem. anal.: calcd for C$_{31}$H$_{34}$O$_5$: %C 76.52, %H 7.04; found: %C 76.62, %H 7.02.

**tert-Butyldiphenylsilyl**

2,3,4-tri-$O$-benzyl-7-(trimethylsilyl)-7,8,9-trideoxy-$\beta$-$d$-gluco- nona-8-enopyranoside.

![Structural diagram](image)

**Oxidation:** Silyl pyranoside 16 (2.08 g, 3.02 mmol) and TEMPO (4.7 mg, 30.2 µmol) were dissolved in dry CH$_2$Cl$_2$ (30 mL) and placed in a water/ice bath. Trichloroisocyanuric acid (0.77 g, 3.32 mmol) was added in one portion and after 15 min TLC (7:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.5) and formation of a new product ($R_f$ 0.4). Mixture was filtered through a Celite pad, diluted with Et$_2$O (30 mL), and washed with: 5% Na$_2$S$_2$O$_3$ (10 mL), 1M NaOH (25 mL), 1M sulfuric acid (25 mL), water (25 mL), brine (25 mL), and concentrated. The residue was dissolved in toluene (50 mL) and evaporated to afford crude aldehyde.

** Allylboronation:** Crude aldehyde was dissolved in dry toluene (30 mL) to which pinacol (E)-1-(trimethylsilyl)-1-propene-3-boronate (0.75 g, 3.02 mmol) was added. The mixture was stirred for 4 days after which TLC (7:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.4) and formation of a two new products ($R_f$ 0.5 and 0.6). Solution was passed through a column of silica and concentrated to afford crude silanol as a mixture of anti diastereomers.
**tert-Butyldiphenylsilyl**

2,3,4-tri-\(O\)-benzyl-6,7,8,9-tetrae oxy-\(\beta\)-\(D\)-gluco-nonadi-6(E),8-enopyranoside (18).

![Chemical structure of 18](image)

Procedure as described for the synthesis of 10 to afford 18 (71% yield from 16) as a colorless oil.

\([\alpha]^{20}_D = 37.3\ (c\ 0.50,\ CHCl_3)\);

\(^1H\) NMR \(\delta\ 7.75–7.63\ (m, 5H,\ arom.),\ 7.44–7.16\ (m, 20H,\ arom.),\ 6.21\ (dt,\ J = 16.8, 10.5\ Hz,\ 1H,\ H-8),\ 5.88\ (dd,\ J = 15.4, 10.6\ Hz,\ 1H,\ H-7),\ 5.56\ (dd,\ J = 15.4, 5.3\ Hz,\ 1H,\ H-6),\ 5.07\ (d,\ J = 11.0\ Hz,\ 1H,\ OCH_2Ph),\ 5.03\ (m,\ 2H,\ H-9\ and\ H-9'),\ 4.88–4.83\ (m,\ 2H,\ 2\times OCH_2Ph),\ 4.77\ (d,\ J = 10.9\ Hz,\ 1H,\ OCH_2Ph),\ 4.72\ (d,\ J = 10.9\ Hz,\ 1H,\ OCH_2Ph),\ 4.61\ (dd,\ J = 5.4\ Hz,\ 1H,\ H-1),\ 4.51\ (d,\ J = 10.9\ Hz,\ 1H,\ OCH_2Ph),\ 3.53\ (m,\ 2H,\ H-2\ and\ H-3),\ 3.42\ (dd,\ J = 9.0, 5.3\ Hz,\ 1H,\ H-5),\ 3.26\ (m,\ 1H,\ H-4),\ 1.12\ (s,\ 9H,\ OSiPh_2C(CH_3)_3);\)

\(^{13}C\) NMR \(\delta\ 138.6,\ 138.5\ and\ 138.0\ (quat.\ benzyl),\ 136.5\ (C-8),\ 136.0,\ 135.9,\ 133.7\ and\ 132.8\ (arom.),\ 132.3\ (C-7),\ 129.7\ and\ 129.5\ (arom.),\ 129.4\ (C-4),\ 128.3–127.3\ (arom.),\ 117.5\ (C-9),\ 98.0\ (C-1),\ 84.6\ (C-3),\ 84.0\ (C-2),\ 82.6\ (C-4),\ 75.7\ and\ 2\times 75.0\ (OCH_2Ph),\ 74.3\ (C-5),\ 27.0\ (OSiPh_2C(CH_3)_3),\ 19.1\ (OSiPh_2C(CH_3)_3);\)

HRMS: calcd for C_{46}H_{50}O_5NaSi [M+Na]^+: 733.3325; found: 733.3322;

elem. anal.: calcd for C_{46}H_{50}O_5Si: %C 77.71, %H 7.09; found: %C 77.90, %H 7.10.

**tert-Butyldiphenylsilyl**

2,3,4-tri-\(O\)-benzyl-6,7,8,9-tetrae oxy-\(\beta\)-\(D\)-gluco-nonadi-6(Z),8-enopyranoside (19).

![Chemical structure of 19](image)

Procedure as described for the synthesis of 11 to afford 19 (76% yield from 16) as a colorless oil.

\([\alpha]^{21}_D = -22.9\ (c\ 0.50,\ CHCl_3)\);

\(^1H\) NMR \(\delta\ 7.69–7.66\ (m, 5H,\ arom.),\ 7.39–7.34\ (m, 3H,\ arom.),\ 7.30–7.20\ (m, 15H,\ arom.),\ 7.18–7.15\ (m, 2H,\ arom.),\ 6.45\ (dt,\ J = 16.7, 10.6\ Hz,\ 1H,\ H-8),\ 6.12\ (t,\ J = 11.0\ Hz,\ 1H,\ H-7),\ 5.30\ (t,\ J = 16.7,\ 1H,\ H-6),\ 5.24\ (d,\ J = 10.0\ Hz,\ 1H,\ H-9'),\ 5.11\ (d,\ J = 10.0\ Hz,\ 1H,\ H-9),\ 5.02\ (d,\ J = 11.1
Hz, 1H, OCH$_2$Ph), 4.84 (d, J = 11.1 Hz, 2H, 2×OCH$_3$Ph), 4.76 (d, J = 10.9 Hz, 1H, OCH$_3$Ph), 4.62–4.54 (m, 3H, H=1 and 2×OCH$_3$Ph), 3.86 (t, J = 9.1 Hz, 1H, H-5), 3.56–3.51 (m, 2H, H-2 and H-3), 3.37–3.33 (m, 1H, H-4), 1.10 (s, 9H, OSiPh$_2$C(CH$_3$)$_3$); 
13C NMR δ 138.7, 138.5 and 138.0 (quat. benzyl), 136.0, 135.8, 133.3, 133.2 (arom.), 133.0 (C-7), 132.7 (C-8), 129.6, 129.6 and 129.6–128.10 (arom.), 128.0 (C-6), 127.9–127.30 (arom.), 119.3 (C-9), 97.7 (C-1), 84.5 (C-3), 83.8 (C-2), 82.5 (C-4), 75.7 and 2×75.0 (OCH$_3$Ph), 71.2 (C-5), 27.0 (OSiPh$_2$C(CH$_3$)$_3$), 19.2 (OSiPh$_2$C(CH$_3$)$_3$); 
HRMS: calcd for C$_{46}$H$_{50}$O$_5$NaSi [M+Na]$^+$: 733.3325; found: 733.3339; 
elem. anal.: calcd for C$_{46}$H$_{50}$O$_5$Si: %C 77.71, %H 7.09; found: %C 77.77, %H 7.18.

2,3,4-Tri-O-benzyl-6,7,8,9-tetradeoxy-D-gluco-nonadi-6(E),8-enopyranose (12)

From 10 (hydrolysis): Methyl pyranoside 10 (1.68 g, 3.45 mmol) was dissolved in AcOH (35 mL) to which 2M triflic acid (12 mL) was added. Solution was stirred at 80°C for 2 h after which TLC (5:1 hexanes-EtOAc) indicated formation of a new product ($R_f$ 0.3); unreacted substrate ($R_f$ 0.6) was also observed. Saturated NaHCO$_3$ (15 mL) and xylene (50 mL) were added and whole mixture was concentrated. The residue was dissolved in Et$_2$O (100 mL) and washed with 1M NaOH (50 mL), water (50 mL), and brine (50 mL), dried, concentrated, and the product was isolated by flash chromatography (9:1→7:1→5:1→3:1 hexanes-EtOAc) to afford 12 (0.41 g, 25% yield) as a white amorphous solid.

From 18 (desilylation): To a solution of silyl pyranoside 18 (1.14 g, 1.60 mmol) in THF (16 mL) and AcOH (140 μL, 24.1 mmol) a solution of TBAF in THF (1.0M, 2.4 mL) was added. After 6 h TLC (3:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.7) and formation of new two products ($R_f$ 0.3 and 0.4). Xylene (16 mL) was added, mixture was concentrated, and the residue was purified by flash chromatography (9:1→7:1→5:1→4:1 hexanes-EtOAc) to afford 12 (0.88 g, 86% yield) as a white amorphous solid.

$\alpha/\beta$ Ratio = 1.4:1 (by NMR – see page SII-5)

$^1$H NMR δ 7.40–7.18 (m, 30H, arom.), 6.41–6.28 (m, 4H, H-7α, H-7β, H-8α and H-8β), 5.72–5.64 (m, 2H, H-6α and H-6β), 5.26–5.11 (m, 5H, H-9α, H-9β, H-9’α, H-9’β and H-1α), 4.95–4.82 (m, 5H, 5×OCH$_3$Ph), 4.79–4.68 (m, 5H, H-1β and 4×OCH$_3$Ph), 4.58 (dd, J = 10.6, 2.7 Hz, 1H,
OCH$_2$Ph), 4.41 (dd, J = 9.8, 7.1 Hz, 1H, H-5α), 3.96 (t, J = 9.3 Hz, 1H, H-3α), 3.86 (dd, J = 9.7, 6.8 Hz, 1H, H-5β), 3.65 (t, J = 9.1 Hz, 1H, H-3β), 3.55 (dd, J = 9.5, 3.6 Hz, 1H, H-2α), 3.39 (dd, J = 9.3, 7.7 Hz, 1H, H-2β), 3.33 (t, 1H, J = 9.3 Hz, H-4β), 3.26 (m, 2H, H-4α and OH-β), 2.95 (s, 1H, OH-α);

$^{13}$C NMR δ 138.6, 138.5, 138.3, 137.9 and 2×137.80 (quat. benzyl), 136.2 (C-8α), 136.1 (C-8β), 2×134.1 (C-7α and C-7β), 130.1 (C-6α and C-6β), 128.5–127.6 (arom.), 118.5 (C-9α), 118.2 (C-9β), 97.3 (C-1β), 91.2 (C-1α), 84.2 (C-3β), 83.1 (C-2β), 82.1 (C-4α), 82.0 (C-4β), 81.3 (C-3α), 80.0 (C-2α), 2×75.8 (OCH$_2$Ph), 75.5 (C-5β), 2×75.2, 74.8 and 73.3 (OCH$_2$Ph), 71.2 (C-5α);

HRMS: calcd for C$_{30}$H$_{32}$O$_5$Na [M+Na]$^+$: 495.2142; found: 495.2112;

elem. anal.: calcd for C$_{30}$H$_{32}$O$_5$Si: %C 76.25, %H 6.83; found: %C 76.03, %H 6.78.

2,3,4-Tri-O-benzyl-6,7,8,9-tetradeoxy-D-gluco-nonadi-6(Z),8-enopyranose (13)

From 11: Procedure as described for the synthesis of 10. Pyranoside 11 (1.70 g, 3.50 mmol) afforded 13 (0.38 g, 23% yield) as white amorphous solid.

From 19: Procedure as described for the synthesis of 18. Pyranoside 19 (1.41 g, 1.99 mmol) afforded 13 (0.79 g, 84% yield) as white amorphous solid.

$\alpha/\beta$ Ratio = 1.4:1 (by NMR – see page SII-6)

$^1$H NMR δ 7.37–7.18 (m, 30H, arom.), 6.74 (m, 2H, H-8α and H-8β), 6.26 (m, 2H, H-7α and H-7β), 5.45 (dd, J = 10.1, 9.3 Hz, 1H, H-6β), 5.39 (t, J = 9.8 Hz, 1H, H-6α), 5.31 (t, J = 15.0 Hz, 2H, H9’α and H-9’β), 5.22 (t, J = 10.3 Hz, 2H, H-9α and H-9’β), 5.18 (t, J = 3.0 Hz, 1H, H-1α), 4.95–4.75 (m, 9H, H-1β, H-5 and 7×OCH$_2$Ph), 4.71–4.62 (m, 5H, 5×OCH$_2$Ph), 4.31 (t, J = 9.1 Hz, 1H, H-5β), 3.98 (t, J = 9.2 Hz, 1H, H-3α), 3.67 (t, J = 9.1 Hz, 1H, H-3β), 3.56 (dd, J = 9.5, 3.6 Hz, 1H, H-2α), 3.41–3.37 (m, 2H, H-2β and H-4β), 3.31 (t, J = 9.4 Hz, 1H, H-4α), 3.15 (d, J = 5.1 Hz, 1H, β-OH), 2.91 (d, J = 2.5 Hz, 1H, α-OH);

$^{13}$C NMR δ 138.7, 138.5, 138.3, 138.0, 2×137.8 (quat. benzyl), 134.1 (C-7α), 133. 8 (C-7β), 132.5 (C-8α), 132.3 (C-8β), 128.5–127.5 (C-6α, C-6β and arom.), 120.2 (C-9β), 119.9 (C-9α), 97.2 (C-1β), 91.3 (C-1α), 84.2 (C-3β), 83.0 (C-2β), 82.1 (C-4α), 82.0 (C-4β), 81.2 (C-3α), 79.9 (C-2α), 2×75.8, 75.3, 74.8 and 73.4 (OCH$_2$Ph), 71.5 (C-5β), 67.0 (C-5α);

HRMS: calcd for C$_{30}$H$_{32}$O$_5$Na [M+Na]$^+$: 495.2142; found: 495.2149;
To a solution of the pyranose 12 (0.75 g, 1.59 mmol) in pyridine (16 mL), NH₂OH.HCl (0.33 g, 4.76 mmol) was added and the mixture was stirred at rt. After 18 h TLC (3:1 hexanes-EtOAc) indicated disappearance of the starting material (Rf 0.5 and 0.4) and formation of two new products (Rf 0.3 and 0.2). The mixture was diluted with xylene (64 mL) and concentrated. The residue was dissolved in Et₂O (25 mL), washed with 1M sulfuric acid (10 mL), water (10 mL), and brine (10 mL), dried concentrated, and the product was purified by flash chromatography (7:1 → 5:1 → 4:1 → 3:1 hexanes-EtOAc) to afford 20 (0.91 g, 82% yield) as a white amorphous solid.

E/Z Ratio = 3.5:1 (by NMR – see page SII-10).

¹H NMR only diagnostic signals: δ 7.47 (d, J = 7.7 Hz, 1H, H-1 anti-oxime), 6.95 (d, J = 6.4, 0.4H, H-1 syn-oxime) for full spectrum see page SII-10;

¹³C NMR δ 151.8 (C-1 syn-oxime), 151.0 (C-1), 149.8 (C-1 anti-oxime), 138.5, 138.4, 138.1, 2×138.0, 137.8, 137.7, 137.6, 137.5, 137.4, 137.3, 137.1 and 2×137.0 (quat. benzyl), 136.4, 136.3, 136.2, 136.0, 135.8, 134.4, 133.8, 132.7, 132.6, 132.4, 132.3, 130.5 and 129.6 (C-6, C-7 and C-8), 128.6–127.3 (C-8 and arom.), 119.4, 118.5, 118.1, 117.7 and 117.5 (C-9), 91.6, 87.7, 85.6, 82.5, 82.2, 82.0, 81.4, 81.3, 80.5, 79.7, 79.6, 79.2, 78.7, 77.5, 77.2, 76.5, 76.3 (CH-OBn), 75.8, 75.6, 2×75.2, 74.9, 74.6, 74.2 and 2×73.8 (OCH₂Ph), 73.2 (CH-OBn), 2×73.1 and 72.1 (OCH₂Ph), 71.9 (CH-OBn), 71.6 (OCH₂Ph), 71.4 (CH-OBn), 71.3 (OCH₂Ph), 70.8 (CH-OBn), 70.5 (OCH₂Ph), 70.3 (CH-OBn);

HRMS: calcd for C₃₀H₃₃NO₅Na [M+Na]⁺: 510.2251; found: 510.2237;

elem. anal.: calcd for C₃₀H₃₃NO₅: %C 73.90, %H 6.82, %N 2.87; found: %C 74.06, %H 6.74, %N 2.77.
(E/Z)-2,3,4-Tri-O-benzyl-6,7,8,9-tetradeoxy-β-D-gluco-nonadi-6(Z),8-enopyranose oxime (21)

Procedure as described for the synthesis of 12. Pyranose 13 (0.99 g, 2.19 mmol) afforded 21 (0.83 g, 81% yield) as a colorless oil.

E/Z Ratio = 3.7:1 (by NMR – see page SII-11)

$^1$H NMR only diagnostic signals δ 7.45 (d, J = 7.7 Hz, 3.7H, ), 6.94 (d, J = 6.4 Hz, 1H, C-1 syn-oxime) for full spectrum see page SII-11;

$^{13}$C NMR δ 151.7 (C-1 syn-oxime), 149.9 (C-1 anti-oxime), 138.6, 138.5, 138.2, 138.1, 2×138.0, 137.8, 137.6, 2×137.5, 137.2 and 137.0 (quat. benzyl), 133.9, 133.8, 132.8, 132.4, 132.3, 132.1, 132.0 and 131.8 (C-7 and C-8), 130.2 and 129.8 (C-6), 128.6–127.6 (C-6 and arom.), 120.2, 119.8, 119.6 and 119.3 (C-9), 91.6, 87.8, 85.6, 82.5, 82.3, 81.9, 80.3, 79.9, 79.8, 79.3, 78.6, 77.4 and 75.9 (CH-OBn), 75.8, 75.7, 75.3, 75.3, 74.9, 74.7, 74.4, 74.1, 73.8 and 73.7 (OCH$_2$Ph), 73.0 (CH-OBn), 72.0 and 71.1 (OCH$_2$Ph), 70.3, 67.6, 67.5 and 66.8 (CH-OBn);

HRMS: calcd for C$_{30}$H$_{33}$NO$_5$Na [M+Na]$^+$: 510.2251; found: 510.2249;

elem. anal.: calcd for C$_{30}$H$_{33}$NO$_5$: %C 73.90, %H 6.82, %N 2.87; found: %C 73.96, %H 6.89, %N 2.84.

Oxazolines 24a and 24b

Oxime 20 (0.48 g, 0.98 mmol) was dissolved in MeOH (6 mL) to which trifluoroacetic acid (15 μL) was added. A solution of (diacetoxyiodo)benzene (0.35 g, 1.08 mmol) in MeOH (3 mL) was added dropwise via a syringe pump within 0.5 h and the mixture was stirred at rt. After 18 h TLC (2:1 hexanes-EtOAc) indicated disappearance of the starting material ($R_f$ 0.4) and formation of two new products ($R_f$ 0.6 and 0.3). The mixture was diluted with toluene (10 mL) and concentrated. Small sample was filtered through a short pad of silica and analysed by HPLC. The rest of the residue
was purified by flash chromatography (5:1→4:1→3:1→2:1 hexanes-EtOAc) to afford a mixture of 24a (285.5 mg, 60% yield) and 24b (71.4 mg, 15% yield) both as a colorless oil.

Diastereoisomeric ratio 81:19 (by HPLC – see page SI-14).

**MAJOR (24a):**

\[ \alpha \] \text{D}^1 = -27.2 (c 0.50, CHCl3);

$^1$H NMR $\delta$ 7.41–7.10 (m, 15H, arom.), 5.84 (ddd, $J = 17.1, 10.3, 7.5$ Hz, 1H, H-8), 5.39 (d, $J = 17.1$ Hz, 1H, H-9'), 5.20 (d, $J = 10.3$ Hz, 1H, H-9), 4.97 (t, $J = 7.5$ Hz, 1H, H-7), 4.70 (d, $J = 10.9$ Hz, 1H, OCH$_2$Ph), 4.59 (m, 2H, 2×OCH$_2$Ph), 4.45 (d, $J = 11.9$ Hz, 1H, OCH$_2$Ph), 4.41 (m, 2H, H-2 and OCH$_2$Ph), 4.33(d, $J = 10.9$ Hz, 1H, OCH$_2$Ph), 4.13 (t, $J = 3.0$ Hz, 1H, H-3), 3.93 (dd, $J = 10.4, 8.2$ Hz, 1H, H-5), 3.81 (t, $J = 3.0$ Hz, 1H, H-4), 3.37 (dt, $J = 7.5, 10.4$ Hz, 1H, H-6), 2.39 (d, $J = 11.4$ Hz, 1H, OH);

$^{13}$C NMR $\delta$ 155.4 (C-1), 137.5, 137.3 and 137.1 (quat. benzyl), 136.0 (C-8), 128.5–127.8 (arom.), 117.6 (C-9), 86.0 (C-7), 78.5 (C-4), 74.4 (C-3), 72.3 and 72.0 (OCH$_2$Ph), 71.9 (C-5), 71.2 (OCH$_2$Ph), 70.5 (C-2), 54.7 (C-6);

HRMS: calcd for C$_{30}$H$_{31}$NO$_5$Na [M+Na]$^+$: 508.2095; found: 508.2106;

elem. anal.: calcd for C$_{30}$H$_{31}$NO$_5$: %C 74.21, %H 6.43, %N 2.88; found: %C 73.97, %H 6.43, %N 2.67.

Structure of product was established by NOE correlations:

![Significant NOESY interactions](image)

The bold letter X indicates the significant NOE interactions:

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SI-13
MINOR (24b):

$^1$H NMR $\delta$ 7.42–7.24 (m, 15H, arom.), 5.91 (ddd, $J = 17.3, 10.2, 7.5$ Hz, 1H, H-8), 5.38 (dt, $J = 17.3, 1.0$ Hz, 1H, H-9), 5.25 (dt, $J = 10.2, 1.0$ Hz, 1H, H-9’), 5.16 (t, $J = 8.3$ Hz, 1H, H-7), 5.09 (d, $J = 11.6$ Hz, 1H, OCH$_2$Ph), 4.95 (d, $J = 10.7$ Hz, 1H, OCH$_2$Ph), 4.81 (d, $J = 10.7$ Hz, 1H, OCH$_2$Ph), 4.76–4.67 (m, 3H, 3×OCH$_2$Ph), 4.27 (dd, $J = 8.9, 1.1$ Hz, 1H, H-2), 4.03 (m, 2H, H-3 and H-4), 3.52 (dd, $J = 9.3, 2.9$ Hz, 1H, H-5), 2.94 (dd, $J = 8.3, 2.9$ Hz, 1H, H-6), 2.64 (s, 1H, OH);

$^{13}$C NMR $\delta$ 155.1 (C-1), 138.4, 137.8 and 137.5 (quat. benzyl), 135.7 (C-8), 128.5–127.7 (arom.), 118.4 (C-9), 82.0 (C-5), 81.9 (C-3 or C-4), 81.8 (C-7), 77.2 (C-2), 76.3, 73.4 and 73.2 (OCH$_2$Ph), 66.3 (C-3 or C-4), 55.6 (C-6).

HRMS: calcd for C$_{30}$H$_{31}$NO$_5$Na [M+Na]$^+$: 508.2095; found: 508.2101;

elem. anal.: calcd for C$_{30}$H$_{31}$NO$_5$: %C 74.21, %H 6.43, %N 2.88; found: %C 74.00, %H 6.43, %N 2.72.

Structure of product was established by NOE correlations:

**Significant NOESY interactions**

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Oxazolines 25a and 25b.

Procedure as described for the synthesis of 20. Oxime 21 (433.5 mg, 0.89 mmol) afforded a mixture of diastereisomers 25a (293.6 mg, 68% yield) as a colorless oil and 25b (18.6 mg, 3% yield) as a amorphous solid.

Diastereomeric ratio 95:5 (by HPLC – see page SI-16).

**MAJOR (25a):**

$[\alpha]_{D}^{21} = 76.3$ (c 0.50, CHCl$_3$);

$^1$H NMR $\delta$ 7.40–7.13 (m, 15H), 6.01 (ddd, J = 17.1, 10.5, 6.5 Hz, 1H, H-8), 5.45 (d, J = 17.1, 1H, H-9), 5.32 (d, J = 10.5 Hz, 1H, H-9’), 5.17 (dd, J = 11.0, 6.5 Hz, 1H, H-7), 4.71 (d, J = 11.0 Hz, 1H, OCH$_3$Ph), 4.62 (m, J = 11.9 Hz, 1H, OCH$_3$Ph), 4.60 (d, J = 12.1 Hz, 1H, OCH$_3$Ph), 4.46 (d, J = 11.9 Hz, 1H, OCH$_3$Ph), 4.40 (m, 2H, H-2 and OCH$_3$Ph), 4.34 (d, J = 11.0 Hz, 1H, OCH$_3$Ph), 4.12
(t, J = 3.2 Hz, 1H, H-3), 4.07 (td, J = 10.8, 3.2 Hz, 1H, H-5), 3.80 (t, J = 3.2 Hz, 1H, H-4), 3.72 (t, J = 10.8 Hz, 1H, H-6), 2.40 (d, J = 10.8 Hz, 1H, OH);

$^{13}$C NMR $\delta$ 154.9 (C-1), 137.5, 137.4 and 137.1 (quat. benzyl), 132.4 (C-8), 128.5–127.7 (arom.), 118.4 (C-9), 82.7 (C-7), 78.4 (C-4), 74.4 (C-3), 72.1, 72.0 and 71.0 (OCH$_2$Ph), 70.4 (C-2), 67.4 (C-5), 51.7 (C-2);

HRMS: calcd for C$_{30}$H$_{31}$NO$_5$Na [M+Na]$^+$: 508.2095; found: 508.2100;

elem. anal.: calcd for C$_{30}$H$_{31}$NO$_5$: %C 74.21, %H 6.43, %N 2.88; found: %C 74.35, %H 6.49, %N 2.76.

Structure of product was established by NOE correlations:

![Diagram of molecule]

Significant NOESY interactions

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MINOR (25b):

$^1$H NMR $\delta$ 7.42–7.25 (m, 15H), 6.36 (ddd, $J$ = 17.4, 10.2, 8.3 Hz, 1H, H-8), 5.42 (d, $J$ = 17.3 Hz, 1H, H-9), 5.38 (d, $J$ = 10.3 Hz, 1H, H-9’), 5.06 (d, $J$ = 11.8 Hz, 1H, OCH$_2$Ph), 5.00 (dd, $J$ = 8.3, 10.9 Hz, 1H, H-7), 4.95 (d, $J$ = 10.7 Hz, 1H, OCH$_2$Ph), 4.80 (d, $J$ = 10.7 Hz, 1H, OCH$_2$Ph), 4.71–4.66 (m, 3H. 3×OCH$_2$Ph), 4.38 (d, $J$ = 8.4 Hz, 1H, H-5), 4.06–4.02 (m, 2H, H-3 and H-5), 3.49 (dd, $J$ = 9.1, 2.2 Hz, 1H, H-4), 3.05 (d, $J$ = 11.0 Hz, 1H, H-6), 2.39 (s, 1H, OH);

$^{13}$C NMR $\delta$ 155.2 (C-1), 138.4, 137.8 and 137.5 (quat. benzyl), 132.5 (C-8), 128.5–127.7 (quat. benzyl), 120.8 (C-9), 83.4 (C-7), 82.9 (C-3), 81.9 (C-4), 77.5 (C-2), 76.3, 73.0 and 72.7 (OCH$_2$Ph), 66.7 (C-5), 53.3 (C-2);

HRMS: calcd for C$_{30}$H$_{31}$NO$_5$Na [M+Na]$^+$: 508.2095; found: 508.2105.
Structure of product was established by NOE correlations:

Significant NOESY interactions

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<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-3/H-5</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-4</td>
<td>X</td>
<td>x</td>
<td>-</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-6</td>
<td>X</td>
<td>x</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>H-7</td>
<td>x</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>H-8</td>
<td>x</td>
<td></td>
<td></td>
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</tbody>
</table>

The bold letter X indicates the significant NOE

Diastereometric ratio was determined by HPLC analysis using RP-18 column (MeCN:H$_2$O 70:30, flow rate 0.750 ml/min, $\lambda = 254$ nm):

<table>
<thead>
<tr>
<th>compound</th>
<th>time [min]</th>
<th>area</th>
<th>area%</th>
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<tbody>
<tr>
<td>24b</td>
<td>13.92</td>
<td>33945</td>
<td>5.054</td>
</tr>
<tr>
<td>24a</td>
<td>15.72</td>
<td>637662</td>
<td>94.946</td>
</tr>
</tbody>
</table>
New strategy to sugar dienes, useful building blocks for the synthesis of bicyclic derivatives

Grzegorz Witkowski and Sławomir Jarosz*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warszawa

Supporting Information, part 2

NMR Spectra

* Corresponding author:
Fax: (+48-22) 632-66-81
E-mail: slawomir.jarosz@icho.edu.pl
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