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## Note

# Amphiphilic liposaccharides. Synthesis and reductive cleavage of *C*-allyl, *O*-allyl, and *O*-butenyl glycosyl derivatives

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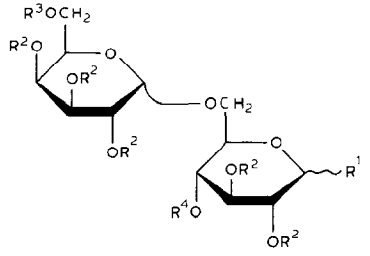
Amphiphilic reagents are useful for the preparation of new biocatalysts[1,2] and we report herein the direct preparation of an additional disaccharide, 6′-octyl-melibiose (**6**). Reductive condensations of reducing sugars with $N^{\alpha}$-Z-L-Lysine proved to be, however, a slow process[1] and, therefore, we investigated the preparation of lipopolysaccharides possessing a free aldehyde function or a hemiacetal group less stable than that of a pyranose. The reductive ozonolysis of alkenyl glycosides has been proposed for the preparation of aldehydoalkyl glycosides[3], and this method was applied to some amphiphilic allyl and butenyl mono- and di-saccharide glycosides, and also to a *C*-allyl liposaccharide.

Tritylation[4] of melibiose (**1**) gave the 6′-trityl derivative **2** and benzylation led to the perbenzylated derivative **3** in 75% yield. After selective cleavage[6] of the



**1** $R^1 = OH, R^2 = R^3 = H$
**2** $R^1 = OH, R^2 = H, R^3 = CPh_3$
**3** $R^1 = OBn, R^2 = Bn, R^3 = CPh_3$
**4** $R^1 = OBn, R^2 = Bn, R^3 = H$
**5** $R^1 = OBn, R^2 = Bn, R^3 = C_8H_{17}$
**6** $R^1 = OH, R^2 = H, R^3 = C_8H_{17}$
**7** $R^1 = OAc, R^2 = Ac, R^3 = C_8H_{17}$
**8** $R^1 = Br(\alpha), R^2 = Ac, R^3 = C_8H_{17}$
**9** $R^1 = OCH_2CH{=}CH_2(\beta), R^2 = Ac, R^3 = C_8H_{17}$
**10** $R^1 = OCH_2CH{=}CH_2(\beta), R^2 = H, R^3 = C_8H_{17}$
**11** $R^1 = OCH_2CH_2CH{=}CH_2(\beta), R^2 = Ac, R^3 = C_8H_{17}$
**12** $R^1 = OCH_2CH_2CH{=}CH_2(\beta), R^2 = H, R^3 = C_8H_{17}$
**13** $R^1 = OCH_2CHO(\beta), R^2 = Ac, R^3 = C_8H_{17}$

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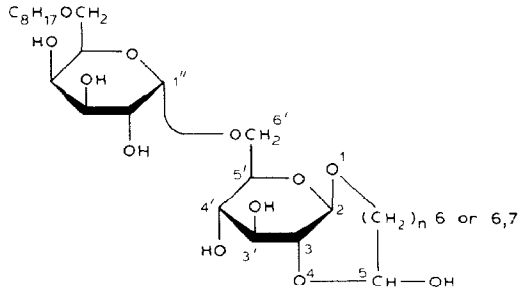
trityl protecting group, the resulting alcohol **4** was alkylated[7] to give ether **5**. Extensive hydrogenolysis afforded 6′-octyl melibiose (**6**) in a 31% overall yield.

Treatment with hydrogen bromide of the peracetylated derivative **7** of **6** afforded bromide **8**, which was condensed in the presence of mercury(II) cyanide[8] with allyl or butenyl alcohol to give **9** and **11**, respectively. Removal of the acetate groups furnished allyl (**10**) and butenyl 6′-octyl-β-melibiosides (**12**), respectively.

Reductive ozonolysis of **9** gave, in 90% yield, **13**, the $^1$H- and $^{13}$C-n.m.r. spectra of which showed the characteristic signals of an aldehyde group at δ 9.65 and 199.47, respectively[10]. Reductive ozonolysis of **10** and **12** having six free hydroxyl groups led to **14** and **15**, respectively, the n.m.r. spectra of which lack these characteristic signals. Moreover, triplets at δ 4.61 and 4.63 in the $^1$H-n.m.r. spectrum of **14** may be attributed to the diastereoisomeric cyclized hemiacetal derivatives, OH-2 being probably involved in the hemiacetal-ring formation[11]. Deacetylation of aldehyde **13** yielded also compound **14**.




**14** n = 1

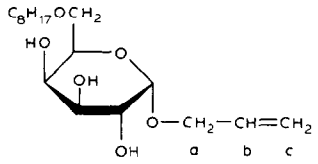
**15** n = 2

Reductive ozonolysis of allyl 6-*O*-octyl-α-D-galactopyranoside (**16**), prepared[8] from 6-*O*-octyl-D-galactose, led to a product (**17**) devoid of the i.r. and n.m.r. spectra characteristic of a free aldehyde group. Furthermore, in the $^1$H-n.m.r. spectrum, a triplet at δ 4.58 (*J* 5.3 Hz), and in the $^{13}$C-n.m.r. spectrum, a signal at δ 103.67 may be assigned respectively to H-5 and C-5 of the hemiacetal form.

Condensation[12,13] in the presence of zinc bromide of 1,2,3,4-tetra-*O*-acetyl-6-*O*-octyl-D-galactose with allyltrimethylsilane gave the *C*-allyl derivative **18** as a mixture of the α and β anomers. Deacetylation and cristallization afforded the pure α anomer **20**. Whereas the reductive ozonolysis of **18** led to the acetylated aldehyde **19** as a mixture of α and β anomers, that of **20** yielded a product which did not display the characteristics of a carbonyl compound. In the $^1$H-n.m.r. spectrum, the signals at δ 5.32 and 5.53 (dd), and in the $^{13}$C-n.m.r. spectra two signals at δ 105.13 and 105.70 could be attributed to the two diastereoisomers of the hemiacetal **21**.

In conclusion, the reductive ozonolysis of *C*-allyl, *O*-allyl, and *O*-butenyl pyranosyl liposaccharides (mono- or di-saccharides) having a neighboring free

hydroxyl group does not give the corresponding free aldehyde but the cyclized hemiacetal derivative.

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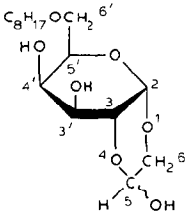


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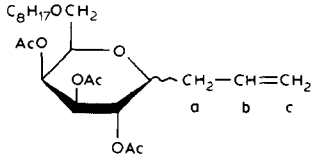


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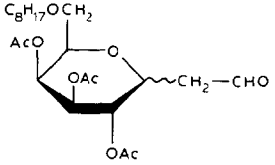


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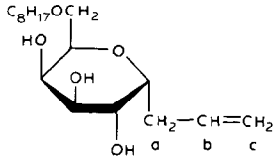


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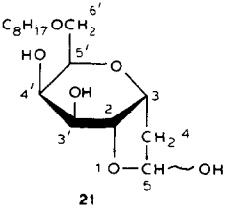


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## EXPERIMENTAL

*General methods.* — Melting points were determined with a FP61 Mettler apparatus. Optical rotations were measured with a Perkin–Elmer polarimeter. $^1$H-N.m.r. spectra were recorded at 90 or 250 MHz, and $^{13}$C-n.m.r. spectra at 20 MHz; unless otherwise stated, the solvent was $CDCl_3$; carbon atoms were numbered a,b,c,d, in the 1-*C*-allyl, 1-*O*-allyl, and 1-*O*-butenyl chains starting from O-1 of the sugar residue. T.l.c. were developed on Silica Gel 60F (Merck) and spots were detected with 10% $H_2SO_4$ by heating. Column chromatography was made on Silica Gel Merck 60 (70–230 mesh). The compounds described subsequently were homogenous on t.l.c., and $R_F$ values were obtained by t.l.c. in the eluent used for the purification by column chromatography.

*6'-O-Tritylmelibiose* (**2**). — Compound **2** was prepared by the method of Adachi and Suami[4]. The product was chromatographed on a silica gel column with 4:1 (v/v) dichloromethane–methanol as eluent to give **2** in 65% yield, $R_F$ 0.30; $^1$H-n.m.r. ($CCl_4$): $\delta$ 3.1–4.2 (13 H), 4.6 (d, $J_{1,2}$ 7 Hz, H-1$\alpha$), 5.2 (d, $J_{1,2}$ 3 Hz, H-1$\beta$), and 7.1–7.5 (m, 15 H, arom.); $^{13}$C-n.m.r. ($CD_3OD$): $\delta$ 64–78 (C cycle),

87.88 (C trityl), 93.59 (C-1$\alpha$), 97.47 (C-1$\beta$), 97.57 (C-1′), and 128.13–144.98 (C arom.).

*Benzyl* O-*(2,3,4-tri*-O-*benzyl-6*-O-*trityl-α*-D-*galactopyranosyl)-(1→6)-2,3,4-tri*-O-*benzyl-α,β*-D-*glucopyranoside* (**3**). — To a solution of 6′-*O*-tritylmelibiose (2.9 g, 5 mmol) in dimethyl sulfoxide (30 mL) was added crushed KOH (5 g). The mixture was maintained at 20° during the dropwise addition of benzyl bromide (8.6 g, 50 mmol) and stirred for 48 h at room temperature. Diethyl ether was added, and the ether solution was decanted, washed with water, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed on a silica gel column with 3:1 pentane–diethyl ether as eluent to give **3** in 75% yield, $R_F$ 0.31; $^1$H-n.m.r.: $\delta$ 3–5.1 (28 H) and 7–7.5 (50 H, arom.); $^{13}$C-n.m.r.: $\delta$ 62.45–75.93 (C cycle), 93.86 (C-1$\alpha$), 96.71 (C-1$\beta$), 101.62 (C-1′), and 126.25–143.20 (C arom.).

*Anal.* Calc. for $C_{80}H_{78}O_{11}$: C, 79.05; H, 6.46. Found: C, 79.05; H, 6.27.

*Benzyl* O-*(2,3,4-tri*-O-*benzyl-α*-D-*galactopyranosyl)-(1→6)-2,3,4-tri*-O-*benzyl-α,β*-D-*glucopyranoside* (**4**). — A solution of **3** (2.4 g, 2 mmol) in dry acetonitrile (30 mL) was maintained under Ar at 0°, and NaI (0.6 g, 4 mmol) and then chlorotrimethylsilane (0.44 g, 4 mmol) were added. The mixture was stirred for 2 h at 0° before addition of diethyl ether. The ether solution was washed with water, and then with $Na_2S_2O_3$ solution, dried, and evaporated. The residue was purified by column chromatography (7:3 pentane–ethyl acetate) to give 1.6 g (85% yield) of **4**, $R_F$ 0.63; $^1$H-n.m.r.: $\delta$ 3.3–5.1 (29 H) and 7.1–7.3 (35 H, arom.); $^{13}$C-n.m.r.: $\delta$ 62.34–76.57 (C cycle), 80.68–82.94 (C benzyl), 94.15 (C-1$\alpha$), 97.75 (C-1$\beta$), 102.40 (C-1′), and 125.93–138.62 (C arom.).

*Anal.* Calc. for $C_{61}H_{64}O_{11}$: C, 75.28; H, 6.62. Found: C, 75.09; H, 6.53.

*Benzyl* O-*(2,3,4-tri*-O-*benzyl-6*-O-*octyl-α*-D-*galactopyranosyl)-(1→6)-2,3,4*-O-*benzyl-α,β*-D-*glucopyranoside* (**5**). — To a solution of **4** (0.97 g, 1 mmol) in *N,N*-dimethylformamide (25 mL) stirred under Ar was slowly added NaH (0.19 g, 5 mmol: 50% in oil). After 1 h at room temperature, octyl bromide (0.73 g, 1.9 mml) was added and the mixture stirred for 24 h. The mixture was poured onto ice and extracted with dichloromethane. The organic layer was washed with water, dried, and evaporated to give a syrup which was purified on a silica gel column with 4:1 (v/v) pentane–ethyl acetate as eluent to give **5** (0.87 g, 80% yield) as a glassy solid, $R_F$ 0.22; $^1$H-n.m.r. ($CCl_4$): $\delta$ 0.8–1.6 (15 H, octyl), 3.3–5.3 (30 H), and 7–7.5 (35 H, arom.); $^{13}$C-n.m.r.: $\delta$ 14.05–30.37 (C octyl), 64.70–76.47 (C cycle), 81.45–83.19 (C benzyl), 94.91 (C-1$\alpha$), 97.92 (C-1$\beta$), 102.32 (C-1′), and 126.00–138.79 (C arom.).

*Anal.* Calc. for $C_{69}H_{80}O_{11}$: C, 76.35; H, 7.43. Found: C, 76.16; H, 7.35.

*6′*-O-*Octylmelibiose* (**6**). — Compound **5** (0.54 g, 0.5 mmol) was dissolved in 1:4 (v/v) oxolan–methanol (50 mL) and 10% Pd–C (50 mg) was added. Hydrogenolysis was effected in a Parr apparatus under $H_2$ (0.3 MPa) for 12 h. The solution was filtered, evaporated, and the residue was purified by column chromatography (3:2 ethyl acetate–methanol) to give **6**, (0.2 g, 92% yield), $R_F$

0.29; $^1$H-n.m.r.: δ 0.8–1.6 (15 H, octyl), 3.1–4.1 (15 H), 4.5 (d, $J_{1,2}$ 8 Hz, H-1α), 4.85 (OH), and 5.1 (d, $J_{1,2}$ 4 Hz, H-1β); $^{13}$C-n.m.r. ($CD_3OD$): δ 14.42–32.95 (C octyl), 67.53–77.96 (C cycle), 93.99 (C-1α), 98.21 (C-1β), and 100.17 (C-1′).

*Anal.* Calc. for $C_{20}H_{38}O_{11}\cdot 0.5\ H_2O$: C, 51.82; H, 8.48. Found: C, 51.87; H, 8.38.

O-*(2,3,4-Tri*-O-*acetyl-6*-O-*octyl-α*-D-*galactopyranosyl)-(1→6)-1,2,3,4-tetra*-O-*acetyl-α,β*-D-*glucopyranose* (**7**). — Compound **6** (1.36 g, 3 mmol) was suspended in acetic anhydride (20 mL), sodium acetate (0.4 g, 5 mmol) was added, and the mixture heated for 2 h at 100°. The solvent was evaporated under diminished pressure, then the residue was dissolved in diethyl ether and washed with water. The ether solution was dried and evaporated to a syrup which was purified on a silica gel column (3:2 pentane–ethyl acetate) to give **7** (1.75 g, 78% yield), $R_F$ 0.42; $^1$H-n.m.r.: δ 0.8–1.6 (15 H, octyl), 1.9–2.2 (21 H, 7 OAc), 3.3–5.3 (15 H), 5.51 (d, $J_{1,2}$ 8 Hz, H-1α), and 6.24 (d, $J_{1,2}$ 4 Hz, H-1β); $^{13}$C-n.m.r.: δ 13.81–31.57 (C octyl), 66.08–76.10 (C cycle), 89.66 (C-1α), 92.29 (C-1β), 96.76 and 97.04 (C-1′).

*Anal.* Calc. for $C_{34}H_{52}O_{18}$: C, 54.54; H, 7.00. Found: C, 54.71; H, 7.21.

O-*(2,3,4-Tri*-O-*acetyl-6*-O-*octyl-α*-D-*galactopyranosyl)-(1→6)-2,3,4-tri*-O-*acetyl-α*-D-*glucopyranosyl bromide* (**8**). — A solution of **7** (1.7 g, 2.3 mmol) in dichloromethane (20 mL) was cooled to 0°, and a saturated solution of HBr in acetic acid (10 mL) was added. After 3 h at 0°, the mixture was poured onto ice. The organic phase was washed with a cooled saturated solution of $NaHCO_3$, dried ($Na_2CO_3$), and evaporated. The residue was rapidly purified by column chromatography (7:3 pentane–ethyl acetate) to give **8** (1.4 g, 79% yield) $R_F$ 0.34; $^1$H-n.m.r.: δ 1.1–1.6 (15 H, octyl), 1.95–2.15 (6 s, 18 H, 6 OAc), 3.3–5.6 (15 H), and 6.6 (d, $J_{1,2}$ 3.97 Hz, H-1β). The bromide **8** was immediately used for glycosylation reactions.

*Allyl* O-*(2,3,4-tri*-O-*acetyl-6*-O-*octyl-α*-D-*galactopyranosyl)-(1→6)-2,3,4-tri*-O-*acetyl-β*-D-*glucopyranoside* (**9**). — To a solution of **8** (1.16 g, 1.5 mmol) in allyl alcohol (5 mL) at 20° under Ar was added $Hg(CN)_2$ (0.42 g, 1.65 mmol). The mixture was stirred for 24 h, and then the alcohol evaporated. The residue was dissolved in dichloromethane, washed with water, and dried. The crude product was applied to a silica gel column and eluted with 3:2 pentane–ethyl acetate to give **9** (0.84 g, 75%), $[\alpha]_{589}^{25}$ + 75°, $[\alpha]_{546}^{25}$ +88° (*c* 2.5, dichloromethane), $R_F$ 0.54; $^1$H-n.m.r.: δ 0.8–1.6 (15 H, octyl), 1.98–2.15 (6 s, 18 H, 6 OAc), 3.3–4.35 (10 H), 4.55 (d, $J_{1,2}$ 8 Hz, H-1α), 4.95–5.5 (9 H), and 5.75–5.95 (m, 1 H, allyl); $^{13}$C-n.m.r.: δ 14.10–31.85 (C octyl), 66.47–73.03 (C cycle), 96.49 (C-1), 99.42 (C-1′), 117.32 ($CH_2$–$CH$=$CH_2$), 133.48 ($CH_2$–$CH$=$CH_2$), and 167.32–169.32 ($COCH_3$).

*Anal.* Calc. for $C_{35}H_{54}O_{17}$: C, 56.29; H, 7.29. Found: C, 56.03; H, 7.24.

*Allyl* O-*(6*-O-*octyl-α*-D-*galactopyranosyl)-(1→6)-β*-D-*glucopyranoside* (**10**). — Compound **9** (0.75 g, 1 mmol) in methanol (90 mL) was deacetylated by addition of sodium methoxide (20 mg). After 2 h at room temperature, methanol was evaporated and the residue purified by chromatography with 4:1 dichloromethane–methanol as eluent to give **10** (0.35 g, 85% yield), $[\alpha]_{589}^{25}$ +39°, $[\alpha]_{546}^{25}$ +46° (*c* 1.1, methanol), $R_F$ 0.60; $^1$H-n.m.r. ($CD_3OD$): δ 0.8–1.6 (15 H octyl), 4.34 (d, $J_{1,2}$ 8 Hz,

H-1), 5.16 and 5.35 (2 H, $CH_2$–CH=C$H_2$), and 5.9–6.1 ($CH_2$–C$H$=$CH_2$); $^{13}$C-n.m.r. ($CD_3OD$): δ 14.44–32.95 (C octyl), 67.40–72.55 (C cycle), 100.00 (C-1), 103.51 (C-1′), 117.53 ($CH_2$–CH=C$H_2$), and 135.63 ($CH_2$–C$H$=$CH_2$).

*Anal.* Calc. for $C_{23}H_{42}O_{11}\cdot 0.5\ H_2O$: C, 54.83; H, 8.60. Found: C, 54.89; H, 8.54.

*3-Butenyl O-(2,3,4-tri-O-acetyl-6-O-octyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-acetyl-β-D-glucopyranoside* (**11**). — A mixture of bromide **8** (0.7 g, 0.9 mmol), 3-buten-1-ol (0.13 g, 1.8 mmol), and $Hg(CN)_2$ (0.28 g, 1.1 mmol) in dry dichloromethane (15 mL) was stirred for 24 h at 20°. The solution was washed with water, dried, and purified by chromatography (7:3 pentane–ethyl acetate) to give **11** (0.38 g, 55% yield), $[\alpha]_{589}^{25}$ +59°, $[\alpha]_{546}^{25}$ +70° (*c* 1.5, dichloromethane), $R_F$ 0.60; $^1$H-n.m.r.: δ 0.8–1.6 (15 H octyl), 1.95–2.15 (6 s, 18 H, 6 OAc), 2.3–2.4 (q, $J_{a,b;b,c}$ 6.8 Hz, H-b), 4.52 (d, $J_{1,2}$ 8 Hz, H-1α), and 5.7–5.85 (ddt, $J_{b,c}$ 6.8, $J_{c,dA}$ 10.4, $J_{c,dB}$ 17.2 Hz, H-c); $^{13}$C-n.m.r.: δ 14.10–38.87 (C octyl), 66.48–73.05 (C cycle), 96.55 (C-1), 100.55 (C-1′), 116.76 ($CH_2$-d), 134.68 (CH-c), and 169.33–170.59 (C$OCH_3$).

*Anal.* Calc. for $C_{36}H_{56}O_{17}$: C, 56.83; H, 7.42. Found: C, 56.84; H, 7.33.

*3-Butenyl O-(6-O-octyl-α-D-galactopyranosyl)-(1→6)-β-D-glucopyranoside* (**12**). — Compound **11** (0.38 g, 0.5 mmol) was deacetylated as described for **10**. Purification by chromatography (17:3 dichloromethane–methanol) gave **12** (0.22 g, 88% yield), m.p. 130°, $[\alpha]_{589}^{25}$ +30°, $[\alpha]_{546}^{25}$ +35° (*c* 2, methanol), $R_F$ 0.36; $^1$H-n.m.r. ($CD_3OD$): δ 0.8–1.7 (15 H octyl), 2.3–2.45 (q, $J_{a,b;b,c}$ 6.8 Hz, H-b), 4.3 (d, $J_{1,2}$ 7.7 Hz, H-1), and 5.75–5.95 (ddt, $J_{b,c}$ 6.8, $J_{c,dA}$ 17.2, $J_{c,dB}$ 10.4 Hz, H-c); $^{13}$C-n.m.r. ($CD_3OD$): δ 14.44–35.29 (C octyl), 67.58–72.59 (C cycle), 100.08 (C-1), 104.48 (C-1′), 116.88 (C-d), and 136.26 (C-c).

*Anal.* Calc. for $C_{24}H_{44}O_{11}$: C, 56.67; H, 8.72. Found: C, 56.63; H, 8.81.

*Reductive ozonolysis; general procedure.* — A solution of the unsaturated melibioside (**9, 10** or **12**; 1 mmol) in dry methanol (10 mL) was cooled to −78° under Ar and treated with $O_3$ until a grey-blue color persisted. The mixture was stirred for a further 15 min. Then an Ar stream was passed through the solution to eliminate excess of $O_3$. Triphenylphosphine (2 mmol) was slowly added and the solution was slowly warmed to room temperature. The stirring was continued for 2 h at room temperature to reduce the ozonide. Triphenylphosphine oxide was filtered and the filtrate evaporated.

*Formylmethyl O-(2,3,4-tri-O-acetyl-6-O-octyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-acetyl-β-D-glucopyranoside* (**13**). — After reductive ozonolysis of **9** (0.15 g, 0.2 mmol), the residue was purified by chromatography (1:1 pentane–ethyl acetate) to give **13** (0.13 g, 90% yield), $R_F$ 0.38; $^1$H-n.m.r.: δ 0.85–1.6 (15 H octyl), 1.98–2.12 (6 s, 18 H, 6 OAc), 4.61 (d, $J_{1,2}$ 7.9, H-1), and 9.65 (CHO); $^{13}$C-n.m.r.: δ 14.10–31.89 (C octyl), 66.36–73.80 (C cycle), 96.66 (C-1), 100.69 (C-1′), 169.32–170.59 (C$OCH_3$), and 199.47 (CHO).

*O-(6-O-Octyl-α-D-galactopyranosyl)-(1→6)-β-D-glucopyrano[1,2-b]-1,4-dioxan-5-ol* (**14**). — Reductive ozonolysis of **10** (0.13 g, 0.26 mmol), and purification by chromatography (4:1 dichloromethane–methanol) gave **14** (0.1 g, 77%

yield), $R_F$ 0.39; with no characteristic i.r. absorption peak in the carbonyl region of the spectrum; $^1$H-n.m.r. ($CD_3OD$; irradiation used to determine H-6 and H-5): $\delta$ 0.85–1.6 (H octyl), 3.52 and 3.68 (m, H-6a and H-6b), 4.25 and 4.26 (2 d, $J_{2,3}$ 8 Hz, H-2), 4.61 and 4.63 (2 t, $J_{6,5}$ 6 Hz, H-5); $^{13}$C-n.m.r.: $\delta$ 14.43–32.97 (C octyl), 67.45–73.02 (C cycle), 97.51 (C-5), 100.08 (C-2), and 104.74 (C-1″).

*Anal.* Calc. for $C_{22}H_{40}O_{12}$: C, 53.21; H, 8.12. Found: C, 53.47; H, 8.25.

Deacetylation of aldehyde **13** by the usual method, followed by chromatography, gave also the same product **14**.

O-*(6-*O*-Octyl-α-*D*-galactopyranosyl-(1→6)-β-*D*-glucopyrano[1,2-*b*]-1,4-dioxepan-5-ol* (**15**). — Reductive ozonolysis of **12** (0.12 g, 0.23 mmol) gave, after chromatography (4:1 dichloromethane–methanol), **15** (0.11 g, 92% yield), m.p. 73°, $R_F$ 0.41; no characteristic CO i.r. absorption; $^1$H-n.m.r. ($CD_3OD$; decoupling experiments to determine the position of H-5, H-6, and H-7); $\delta$ 0.85–1.6 (H octyl), 1.90 (q, $J_{6,5;7,6}$ 6.3 Hz, H-6), 3.65 and 3.91 (m, H-7a and H-7b), 4.27 (d, $J_{2,3}$ 8 Hz, H-2), and 4.59 (t, $J_{6,5}$ 6 Hz, H-5); $^{13}$C-n.m.r. ($CD_3OD$): $\delta$ 14.47–33.03 (C octyl), 38.11 (C-6), 67.43–72.65 (C cycle), 97.42 (C-5), 100.15 (C-2), and 104.71 (C-1″).

*Anal.* Calc. for $C_{23}H_{42}O_{12}\cdot H_2O$: C, 52.25; H, 8.39. Found: C, 52.37; H, 8.25.

*Allyl 6-*O*-octyl-α-*D*-galactopyranoside* (**16**). — To a solution of 6-*O*-octyl-D-galactose (292 mg, 1 mmol) in allyl alcohol (3 mL) was added Dowex 50W-X8 (200 mg), and the suspension was heated at reflux for 90 min. Dichloromethane was added, and the solution was filtered and evaporated. The residue was chromatographed (9:1 dichloromethane–methanol) to give **16** (150 mg, 45% yield), ratio $\alpha$:$\beta$ = 7:3), $R_F$ 0.44. The $\alpha$ anomer was obtained by cristallization from ethanol, m.p. 127°, $[\alpha]_{589}^{25}$ +107°, $[\alpha]_{546}^{25}$ +126° (*c* 1.3, methanol); $^1$H-n.m.r.: $\delta$ 0.85–1.75 (15 H octyl), 3.3–4.3 (m, 10 H), 5.02 (d, $J_{1,2}$ 3–4 Hz, H-1), 5.1–5.4 (2 H, –CH=C$H_2$), and 5.6–6.1 (–C$H$=CH$_2$); $^{13}$C-n.m.r.: $\delta$ 14.09–31.88 (C octyl), 68.56–73.79 (C cycle), 98.01 (C-1$\alpha$), 102.18 (C-1$\beta$), 117.62 and 117.91 (–CH$_2$–CH=C$H_2$, $\alpha$ and $\beta$), and 134.04 (–CH$_2$–C$H$=CH$_2$).

*Anal.* Calc. for $C_{17}H_{32}O_6$: C, 61.41; H, 9.70. Found: C, 61.16; H, 9.58.

*6-*O*-Octyl-α-*D*-galactopyrano[1,2-*b*]-1,4-dioxan-5-ol* (**17**). — Reductive ozonolysis of **16**, as described above, gave a crude product in which no aldehyde function was detectable by i.r. and n.m.r. spectroscopy. Purification by chromatography (9:1 dichloromethane–methanol) gave **17** (90% yield), $R_F$ 0.42; $^1$H-n.m.r. ($CD_3OD$): $\delta$ 0.85–1.58 (15 H octyl), 3.4–4.2 (m, 10 H), 4.58 (t, $J_{6,5}$ 5.3 Hz, H-5), and 4.96 (d, $J_{2,3}$ 3.6 Hz, H-2); $^{13}$C-n.m.r. ($CD_3OD$): $\delta$ 14.30–32.62 (C octyl), 68.22–72.46 (C cycle and C-6), 100.58 (C-2$\alpha$), and 103.67 (C-5).

*Anal.* Calc. for $C_{16}H_{30}O_7$: C, 57.46; H, 9.04. Found: C, 57.18; H, 8.92.

*3-(2,3,4-Tri-*O*-acetyl-6-*O*-octyl-α,β-*D*-galactopyranosyl)-1-propene* (**18**). — 1,2,3,4-Tetra-*O*-acetyl-6-*O*-octyl-D-galactose (880 mg, 1.91 mmol) was dissolved in allyltrimethylsilane (5 mL). $ZnBr_2$ (1 g, 4.4 mmol) was added and the mixture was heated at reflux for 4 h. The crude product was diluted with ether and washed with water. Purification by chromatography (3:1 pentane–ether) gave **18** a mixture of $\alpha$ and $\beta$ anomers (0.61 g, 72% yield), $R_F$ 0.34; $^1$H-n.m.r.: $\delta$ 0.85–1.6 (15 H octyl),

2.01–2.06–2.13 (3 s, OAc), 1.98–2.04–2.15 (3 s, OAc), 2.2–2.6 (2 H, $CH_2$–CH=$CH_2$), 3.2–3.6 (4 H, $H_2$-6 and 2 H octyl), 3.97 (dt, H-5), 4.33 (q, H-1), 5–5.5 (H-2,3,4 and $CH_2$–CH=$CH_2$), and 5.7–5.9 ($CH_2$–CH=$CH_2$); $^{13}$C-n.m.r.: δ 14.10–36.26 (C octyl and $CH_2$–CH=$CH_2$), 68.46–72.47 (C cycle), 117.21 and 117.52 ($CH_2$–CH=$CH_2$,α,β), 133.66 ($CH_2$–CH=$CH_2$), and 169.86–170.05 ($COCH_3$).

*Anal.* Calc., for $C_{23}H_{38}O_8$: C, 62.42; H, 8.66. Found: C, 62.25; H, 8.87.

*3-(6-*O*-Octyl-α-*D*-galactopyranosyl)-1-propene* (**20**). — Compound **18** was deacetylated with sodium methoxide in methanol for 1 h at room temperature. Cristallization of the crude product in absolute ethanol gave the pure α anomer, m.p. 114°; $^1$H-n.m.r. ($CD_3OD$): δ 0.85–1.65 (15 H, octyl), 2.2–2.5 (2 H, $CH_2$–CH=$CH_2$), 5–5.2 (2 H, $CH_2$–CH=$CH_2$), and 5.8–6.0 (1 H, $CH_2$–CH=$CH_2$); $^{13}$C-n.m.r. ($CD_3OD$): δ 14.14–32.04 (C octyl and $CH_2$–CH=$CH_2$), 68.86–75.93 (C cycle), 116.84 ($CH_2$–CH=$CH_2$), and 135.31 ($CH_2$–CH=$CH_2$).

*Anal.* Calc. for $C_{17}H_{32}O_5$: C, 64.52; H, 10.19. Found: C, 64.36; H, 10.21.

*2-(2,3,4-Tri-*O*-acetyl-6-*O*-octyl-α,β-*D*-galactopyranosyl)ethanal* (**19**). — Reductive ozonolysis of **18** (α and β anomers; 225 mg, 0.51 mmol) gave, after purification by chromatography (2:1 pentane–ether), **19** (160 mg, 71% yield), $R_F$ 0.41; $^1$H-n.m.r.: δ 0.85–1.6 (15 H, octyl), 2.01–2.03–2.12 (3 s, OAc), 1.99–2.04–2.13 (3 s, OAc), 2.8 (2 H, $CH_2$CHO), 3.2–3.6 (4 H, $H_2$-6 and 2 H octyl), 3.8–4.0 (H-5), 4.8–5.5 (5 H), and 9.8 (1 H, CHO); $^{13}$C-n.m.r.: δ 14.12–31.88 (C octyl), 41.58 and 45.75 ($CH_2$CHO,α,β), 67.66–73.34 (C cycle), 169.79–170.04 ($COCH_3$), 198.42 and 198.99 (CHO,α,β).

*Anal.* Calc. for $C_{22}H_{36}O_9$: C, 59.44; H, 8.16. Found: C, 59.50; H, 8.21.

*(6-*O*-Octyl-α-*D*-galactopyrano)[2,1-*b*]oxolan-5-ol* (**21**). — Reductive ozonolysis of **20** (80 mg, 0.25 mmol) under the usual conditions gave, after purification by chromatography (9:1 dichloromethane–methanol), **21** (68 mg, 85% yield), m.p. 105°, $R_F$ 0.38; $^1$H-n.m.r.: ($CD_3OD$): δ 0.85–1.6 (15 H, octyl), 1.85–2.25 (2 H, $H_2$-4), 3.4–4.8 (6 H), 5.32 and 5.53 (dd, 1 H, H-5, α,β anomers); $^{13}$C-n.m.r. ($CD_3OD$): δ 14.34–32.66 (C octyl), 37.02 and 39.70 (C-4), 68.61–75.59 (C cycle), 105.13 and 105.70 (C-5, α,β).

*Anal.* Calc. for $C_{16}H_{30}O_6$: C, 60.34; H, 9.49. Found: C, 60.35; H, 9.38.

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