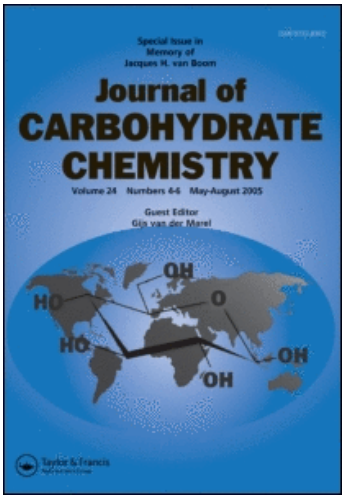

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A SUCROSE-BASED APPROACH TO ENANTIOMERICALLY PURE GLYCEROL DERIVATIVES

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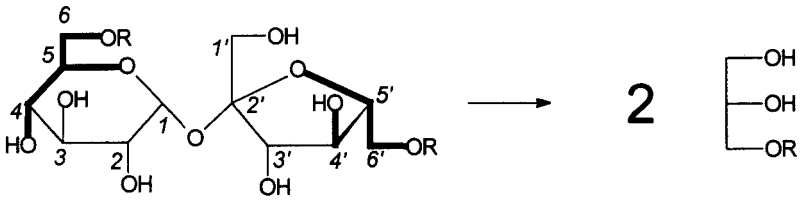
ABSTRACT

Taking advantage of the same configuration present at C-5 and C-5' in sucrose, 6,6'-diprotected sucrose derivatives were transformed into enantiomerically pure glycerol derivatives. This was achieved by oxidative ring cleavage of both the glucopyranosyl ring as well as the fructofuranosyl moiety followed by reduction of the resulting tetraaldehyde and subsequent per-*O*-protection of the resulting pentahydroxy compound. The obtained intermediate was hydrolysed under acidic conditions to furnish two equivalents of partially protected chiral glycerol derivative per molecule of starting material. The efficiencies of sodium metaperiodate and lead tetraacetate as oxidizing agents were compared and the side reactions observed in these procedures were investigated.

INTRODUCTION

Sucrose (**1**) is a large scale commodity and by far the cheapest enantiomerically pure low molecular weight natural product available.[1] Due to its abundance and annual surplus production, many attempts have been made to utilize this disaccharide for the preparation of sophisticated products such as sweeteners and detergents, as well as other potentially useful compounds.[2] Reviews on classical sucrose chemistry as well as on sucrose as an interesting and cheap renewable source of chirality have been published.[3]



Scheme 1

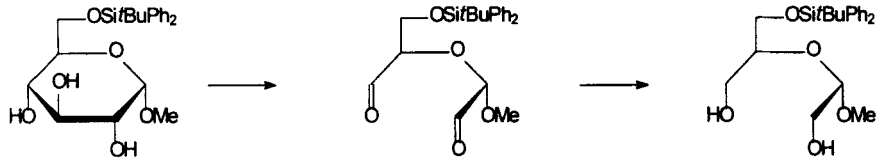
Typical derivatives reported are sucrose esters, oxidation products as well as transglucosylation products such as palatinose or leucrose.[4]

In the course of a programme on potential applications of sucrose as a starting material[5] for interesting organic intermediates, we became interested in 6,6'-dimodified derivatives as precursors of enantiomerically pure glycerol derivatives. The aim of the work was to take advantage of the two three carbon units C-4 to C-6 of both constituents, D-fructose and D-glucose, featuring the same configuration at C-5 (Scheme 1, heavy lines). Such glycerol derivatives are conventionally available from 1,2:5,6-di-*O*-isopropylidene-D-mannitol, a starting material twenty times the price of sucrose on a molar basis.

RESULTS AND DISCUSSION

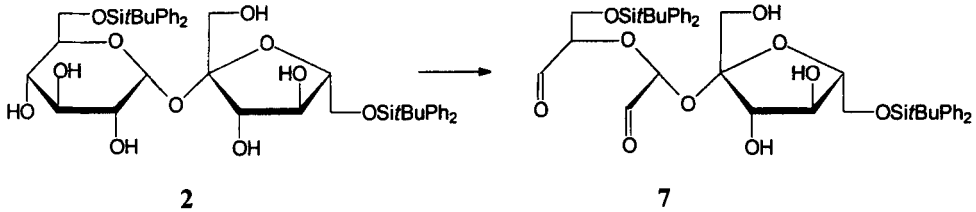
In our initial approach, sucrose was regioselectively *O*-silylated under standard conditions (DMF, imidazole, *tert*-butyldiphenylchlorosilane) to give 6,6'-di-*O*-*tert*-butyldiphenylsilylsucrose[6] (**2**) in fair yield. Treatment of this compound with sodium metaperiodate in a two-phase system of water and diethyl ether did not lead to the desired oxidative ring cleavage products within a reasonable time span. This problem could only be partially overcome by employing wet tetrahydrofuran as the solvent.

Under the conditions employed, only the glucopyranosyl ring was cleaved while the fructofuranose moiety remained intact (Scheme 3). This was also found to be the case in model studies employing 6-*O*-silylated methyl-α-D-glucopyranoside (**3**)[7] which smoothly led to the desired dialdehyde **4** which, in turn, was reduced to diol **5** (Scheme 2).

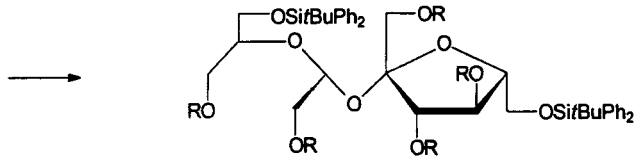


3 4 5

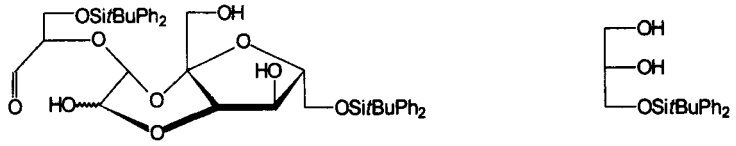
Scheme 2



2 7



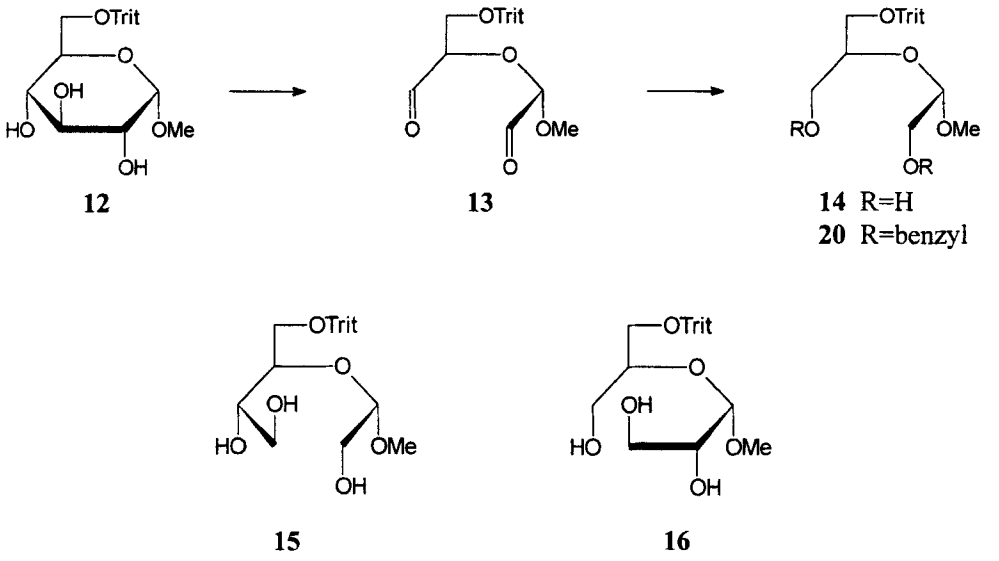
8 R=H
9 R=Ac



6 10

Scheme 3

This result had previously been attributed to intramolecular formation of hemiacetals, such as in structure **6** in Scheme 3, which arise from the reaction of an aldehyde from the former glucose ring and a hydroxyl group in the fructofuranose part, consequently protecting the diol system in this unit from oxidative cleavage.[8] Reduction of the di-aldehyde **7**, obtained from sucrose derivative **2**, furnished penta-ol **8** which was

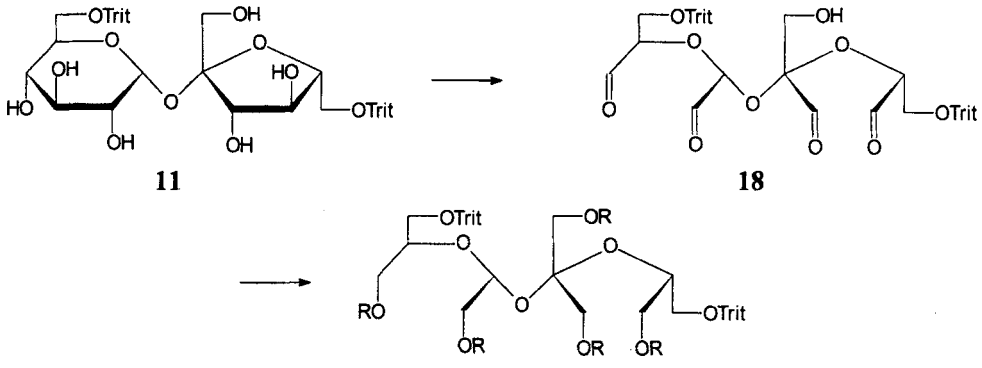


Scheme 4

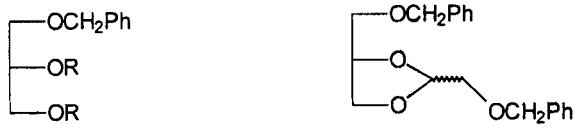
also characterized as the penta-*O*-acetyl derivative **9** (Scheme 3). However, all attempts to liberate the desired glycerol derivative **10**[9] from this intermediate by acidic hydrolysis were unsuccessful. The undesired cleavage of the silyl ether under a variety of conditions proceeded at about the same rate as the acetal hydrolysis.

Following a slightly modified approach in a second set of experiments, 6,6'-di-*O*-tritylsucrose[10] (**11**) was employed as the starting material. Preliminary experiments (Scheme 4) conducted with methyl 6-*O*-trityl-α-D-glucopyranoside (**12**) indicated that cleavage proceeded smoothly in the glucopyranosyl unit leading to dialdehyde **13**. This unstable compound was trapped by conventional reduction with sodium borohydride. The yields of the desired diol **14** did not exceed about 60%. Triols **15** and **16** were detected as side products stemming from incomplete oxidative cleavage under the conditions employed. The same was found for the periodate mediated reaction of sucrose derivative **11**. In addition, side products, such as **17**, the 6,6'-di-*O*-trityl analogue of **7**, were formed in varying amounts.

These difficulties could be avoided by employing lead tetraacetate as the oxidizing agent. Utilising this reagent, complete and smooth ring cleavage could be



Scheme 5



Scheme 6

achieved in model compound **12** as well as in sucrose derivative **11**, in both cases leading to the desired corresponding labile open-chain products **13** and **18**, respectively. From these intermediates, by reduction of the respective carbonyl groups with sodium borohydride in methanol and 1-butanol, diol **14** and penta-ol **19**, respectively, were formed in good yields (Schemes 4 and 5).

Conventional per-*O*-benzylation of glucose derived diol **14** gave the di-*O*-benzyl derivative **20** in high yields. This was hydrolysed to furnish desired (2*R*)-1-*O*-benzylglycerol[11] **21** (Scheme 6) together with one equivalent of 2-benzyloxyacetaldehyde. In good agreement with published values[12] of 17.0°, the optical rotation of the corresponding diacetate **22** in methanol was found to be 16.8°. Comparison of the optical activities of compound **22** and a di-*O*-acetylated sample of

commerically available[13] compound **21** in chloroform gave a value of 14.9° for the former as compared with 14.0° for the per-*O*-acetylated derivative of commercially available standard.

In the case of tetraaldehyde **18**, upon reduction of the aldehyde functions to give **19** and subsequent per-*O*-benzylation, unstable penta-*O*-benzyl intermediate **23** could be prepared in high yield. The hydrolysis of this compound furnished glycerol derivative **21** in 65-70% yield, based on sucrose, exhibiting an optical activity of 14.6° in chloroform. This result nicely matches the values obtained from the methyl-α-D-glucopyranoside based material as well as the commercially aquired sample. In initial hydrolysis experiments employing 4-toluenesulfonic acid in a homogeneous mixture of dichloromethane/methanol/water (1:2:1, v/v/v), compound **24** was formed as a side product in yields of up to 40%. This could be avoided using trifluoroacetic acid as the catalyst and acetonitrile/water (1:1, v/v) as the solvent system. This was also distinctly superior to acidic ion exchange resin in the same solvent mixture.

In conclusion, an interesting new route to enantiomerically pure glycerol derivatives from sucrose is reported which could be developed to rival conventional routes based on 1,2:5,6-di-*O*-isopropylidene-D-mannitol and others[14] in terms of both overall yields as well as optical purities of products. Catalytic procedures for the oxidative ring cleavage not dependent on comparably expensive and/or environmentally questionable reagents such as lead tetraacetate or sodium metaperiodate as well as a variety of additional 6,6'-dimodified sucrose derivatives such as 6,6'-diazido-6,6'-dideoxysucrose[15] as starting materials are currently being investigated.

EXPERIMENTAL

General Methods. Melting points were determined on a Tottoli apparatus (Büchi 300) and are uncorrected. Optical rotations were measured with a JASCO DIP-360 Digital Polarimeter at 589 nm at ambient temp. NMR spectra were recorded at 300.13 or 200 MHz (^{1}H) as well as 75.47 or 50.29 MHz (^{13}C). Residual non-deuterated solvent was used as internal standard for determination of chemical shifts. The signals of protecting groups are in the expected regions and are not listed explicitly. TLC was performed on

precoated aluminum plates (Merck 5554) employing 5% vanillin/sulfuric acid as well as ceric ammonium molybdate as staining agents. For column chromatography, silica gel 60, 230-400 mesh (Merck 9385), was used.

General Procedure for glycol cleavages with sodium metaperiodate. To a 10% solution of the respective starting material in THF, 10 equiv of sodium metaperiodate were added as a saturated aq solution. After complete conversion of the starting material, solids were filtered off and the solution concentrated under reduced pressure. Dichloromethane was added and the organic layer was consecutively washed with 3% aq HCl and saturated aq bicarbonate, dried (sodium sulfate), filtered and concentrated under reduced pressure. The remaining material was immediately used in the next step.

General Procedure for glycol cleavages with lead tetraacetate. To a 5% solution of the starting material in dichloromethane, a molar excess of lead tetraacetate was added and the mixture stirred at ambient temp until TLC indicated completed conversion. Excess oxidant was removed by addition of oxalic acid and subsequent filtration. The organic layer then was washed with saturated aq bicarbonate, dried (sodium sulfate), filtered and concentrated under reduced pressure. The crude product thus obtained was immediately used for the next step.

General Procedure for reduction reactions with sodium borohydride. To a solution of 5 eq of sodium borohydride per free carbonyl group, the respective aldehyde in 1-butanol was added slowly. After completed reaction, acidic ion exchange resin Amberlite IR 120 was added and the mixture stirred until it had reached neutral pH. After filtration, the filtrate was concentrated under reduced pressure, the residue was three times concentrated from methanol to remove boric acid. After chromatographic purification, the resulting material was taken into the respective next step.

General Procedure for *O*-benzylations. To a 5% solution of the starting material in a mixture of DMF/THF 1:1 (v/v), sodium hydride (1.5 eq per free hydroxyl group) was added followed by benzyl bromide (1.35 eq per free hydroxyl group) and the mixture was stirred at ambient temp until the starting material could not be detected by TLC. Excess methanol was added carefully. After 30 min, the reaction mixture was concentrated under reduced pressure. The residue was partitioned between dichloromethane and 3% aq HCl, and the organic layer was washed with 5% aq sodium bicarbonate and dried (sodium

sulfate). After filtration, the filtrate was concentrated under reduced pressure and the remaining material was purified on silica gel or immediately subjected to hydrolysis.

(1*S*)-1-[(2*S*)-1-*tert*-Butyldiphenylsilyloxy-3-hydroxy-2-propyloxy]-1-methoxy-2-hydroxyethane (5). Following the general procedure for the glycol cleavages with metaperiodate, partially protected methyl α-D-glucopyranoside **3** (1.50 g, 3.5 mmol) was cleaved to give intermediate **4**, which was reduced with borohydride according to the general procedure to give open-chain diol **5** (1.3 g, 93%) as a slightly yellow oil: $[\alpha]_D^{20}$ -8.2° (*c* 1.5, chloroform); ^{1}H NMR ($CDCl_3$) δ 4.55 (t, 1 H, J 5.3 Hz), 3.81 (m, 1 H), 3.76-3.54 (m, 6 H), 3.38 (s, 3 H); ^{13}C NMR δ 104.2, 79.5, 64.1, 63.3, 62.7, 55.3.

Anal. Calcd for $C_{22}H_{32}O_5Si$ (404.57): C, 65.31; H, 7.98. Found: C, 65.12; H, 8.09.

(1*R*)-1-[(2*S*)-1-*tert*-Butyldiphenylsilyloxy-3-hydroxy-2-propoxy]-2-hydroxyethyl -6-*O*-*tert*-butyldiphenylsilyl-β-D-fructofuranoside (8). Applying the general procedure for glycol cleavage with metaperiodate to sucrose derivative **2** (820 mg, 1.0 mmol) followed by immediate reduction of the resulting dicarbonyl compound **7** employing the general procedure, after chromatography on silica gel employing petrol ether/ethyl acetate 1:10, v/v, as the eluant, gave product **8** (430 mg, 54%) as a colourless unstable syrup: ^{1}H NMR ($CDCl_3$) δ 5.15 (bs, 1 H), 5.00 (bs, 1 H, OH), 4.65 (bs, 1 H, OH), 4.58 (bs, 1 H, OH), 4.37 (bs, 1 H, OH), 4.12 (bm, 4 H), 3.87 (m, 4 H), 3.50 (m, 4 H); ^{13}C NMR δ 104.0, 98.4, 82.2, 80.0, 79.5, 76.8, 65.6, 64.5, 64.3, 64.1, 62.9.

For analytical purposes, product **8** was per-*O*-acetylated with acetic anhydride in pyridine under standard conditions to give stable derivative **9**: $[\alpha]_D^{20}$ -27.8° (*c* 1.9, chloroform); ^{1}H NMR ($CDCl_3$) δ 5.49 (dd, 1 H, *J* 5.6 Hz, *J* 5.5 Hz), 5.32 (d, 1 H, *J* 5.5 Hz), 5.24 (t, 1 H, *J* 5 Hz), 4.36 (d, 1 H, *J* 12.1 Hz), 4.13 (d, 1 H, *J* 12.1 Hz), 4.10-3.97 (m, 6 H), 3.84 (d, 2 H, *J* 6.4 Hz), 3.61 (d, 2 H, *J* 4.4 Hz).

Anal. Calcd for $C_{53}H_{68}O_{15}Si_2$ (1001.28): C, 63.58; H, 6.84. Found: C, 63.19; H, 6.62.

(1*S*)-1-[(2*S*)-1-Triphenylmethyloxy-3-hydroxy-2-propyloxy]-1-methoxy-2-hydroxyethane (14) and (1*S*)-1-[(2*R*)-3-Benzyloxy-1-triphenylmethyloxy-2-propyloxy]-1-methoxy-2-benzyloxyethane (20). Following the general procedure for the glycol cleavage with metaperiodate, partially protected methyl α-D-glucopyranoside **12** (2.18 g, 5.0 mmol) was cleaved to give intermediate **13**, which was reduced with borohydride

according to the general procedure to give slightly unstable open-chain diol **14** (1.1 g, 54%) after chromatography (petrol ether/ethyl acetate 1:2, v/v) as a faintly yellow syrup which was immediately used in the next step: ^{1}H NMR ($CDCl_3$, after D_2O-exchange) δ 4.57 (t, 1 H, *J* 5.4 Hz), 3.83 (m, 1 H), 3.74 (dd, 1 H, *J* 11.6 Hz, *J* 3.2 Hz), 3.63 (dd, 1 H, *J* 11.6 Hz, *J* 7.6 Hz), 3.58 (d, 2 H, *J* 5.4 Hz), 3.39 (s, 3 H, OMe), 3.26 (dd, 1 H, *J* 10 Hz, *J* 5.4 Hz), 3.21 (dd, 1 H, *J* 10 Hz, *J* 5.4 Hz); ^{13}C NMR δ 104.4, 78.7, 64.3, 63.9, 62.9, 55.4 (OMe).

Following the general procedure for *O*-benzylations, diol **14** (1.00 g, 2.5 mmol) gave di-*O*-benzyl derivative **20** (1.2 g, 86%) after chromatographic purification (petrol ether/ethyl acetate 4:1, v/v): $[\alpha]_D^{20}$ -5.2° (*c* 2.5, chloroform); ^{1}H NMR ($CDCl_3$) d 4.83 (t, 1 H, *J* 5.2 Hz), 4.1 (m, 1 H), 3.68 (d, 2 H, *J* 5.2 Hz), 3.55 (d, 2 H, *J* 5.1 Hz), 3.42 (s, 3 H, OMe), 3.33 (dd, 1 H, *J* 10 Hz, *J* 5.2 Hz), 3.25 (dd, 1 H, *J* 10 Hz, *J* 5.2 Hz); ^{13}C NMR δ 102.2, 76.0, 70.8, 70.4, 64.0, 53.4 (OMe).

Anal. Calcd for $C_{37}H_{36}O_5$ (560.68): C, 79.26; H, 6.47. Found: C, 78.98; H, 6.58.

1,3-Dihydroxy-2-[(2*R*)-3-hydroxy-1-triphenylmethoxy-2-propyloxy]-2- (1*R*)-1-[(2*R*)-3-hydroxy-1-triphenylmethyloxy-2-propyloxy]-2-hydroxyethyloxy -propane (19). Following the general procedures for glycol cleavage with lead tetraacetate and for sodium borohydride reductions, 6,6'-di-*O*-tritylsucrose (**11**, 1.65 g, 2 mmol) gave, after chromatography (petrol ether/ethyl acetate 2:1, v/v), labile compound **19**: ^{13}C NMR ($CDCl_3$) δ 102.8, 97.2, 77.4, 74.1, 65.2, 64.4, 64.3, 64.2, 63.5, 62.3 (2 carbons). Neither before nor after D_2O-exchange, well resolved ^{1}H NMR spectra of this compound could be obtained. Due to the sensitivity of compound **19**, no satisfactory elemental analysis data could be collected.

1,3-Dibenzyloxy-2-[(2*R*)-3-benzyloxy-1-triphenylmethyloxy-2-propyloxy]-2-(1*R*)-1-[(2*R*)-3-benzyloxy-1-triphenylmethoxy-2-propyloxy]-2-benzyloxyethyloxy -propane (23). Following the general procedure for *O*-benzylations, penta-ol **19** (400 mg, 0.5 mmol) was converted into fully protected, labile derivative **23** (520 mg, 83%) which after chromatography (petrol ether/ethyl acetate 10/1, v/v) was obtained as a colourless oil that decomposed at ambient temp: ^{1}H NMR ($CDCl_3$) δ 5.30 (t, 1 H, *J* 5 Hz), 4.25 (m, 1 H), 4.08 (m, 1 H), 3.71 (m, 2 H), 3.66-3.53 (m, 6 H), 3.39 (d, 2 H, *J* 5 Hz), 3.30-3.16 (m, 4 H); ^{13}C NMR δ 101.7, 95.7, 74.5, 72.0, 70.6, 70.5, 70.2, 69.6, 69.5, 63.6, 63.5.

Acidic hydrolysis of compound 23 with 4-toluenesulfonic acid. To a 5% solution of **23** (400 mg, 0.32 mmol) in dichloromethane, about half of its volume of water and 10 eq of 4-toluenesulfonic acid were added and the mixture was homogenized by addition of methanol. The reaction was kept at ambient temp until TLC indicated no further change. After addition of solid sodium bicarbonate, the mixture was concentrated and the products were separated on silica gel to give a diastereomeric mixture of (2*R*/*S*,4*R*)-2,4-dibenzyloxymethyl-1,3-dioxolane (**24**) as a colourless syrup (37 mg, 37%). Data of the predominant diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.13 (t, 1 H, *J* 4 Hz), 4.30 (m, 1 H), 3.97 (dd, 1 H, *J* 8.2 Hz, *J* 6.7 Hz), 3.85 (dd, 1 H, *J* 8.2 Hz, *J* 5.5 Hz), 3.64-3.55 (m, 3 H), 3.48 (dd, *J* 9.9 Hz, 5.9 Hz); ^{13}C NMR δ 103.4, 75.2, 71.0, 70.7, 67.7.

Anal. Calcd for $C_{19}H_{22}O_4$ (314.38): C, 72.59; H, 7.05. Found: C, 72.21; H, 7.20.

(2*R*)-1-*O*-Benzylglycerol (21). A: from 20. To a 3% solution of starting material 19 (280 mg, 0.50 mmol) in wet acetonitrile, trifluoroacetic acid (10 eq) was added and the mixture was stirred at 40 °C until compound **20** could not be detected any more by TLC. Solid sodium bicarbonate was added to neutrality and the solids were filtered. Concentration of the solution under reduced pressure followed by chromatography of the residue led to chiral glycerol derivative **21** (77 mg, 85%) which was isolated as colourless hygroscopic crystals: ^{1}H NMR ($CDCl_3$, after D_2O-exchange) δ 3.87 (m, 1 H, H-2), 3.64 (dd, 1 H, $J_{1,2}$ 3.6 Hz, $J_{1,1'}$ 11.6 Hz, H-1), 3.54 (dd, 1 H, $J_{2,3'}$ 6.1 Hz, H-1'), 3.49 (m, 2 H, H-3,3'); ^{13}C NMR δ 71.7, 70.9, 64.1.

Anal. Calcd for $C_{10}H_{14}O_3$ (182.21): C, 65.92; H, 7.74. Found: C, 65.99; H, 7.95.
Its optical purity was determined from the corresponding per-*O*-acetylated derivative **22**.

B: from 23. To a 2% solution of compound **23** (2.90 g, 2.3 mmol) in wet acetonitrile, trifluoroacetic acid (10 eq) was added and the mixture was kept at 40 °C until all starting material had been consumed. Solid sodium bicarbonate was added to neutralize the catalyst and the mixture was filtered. Concentration of the filtrate under reduced pressure and chromatographic purification of the residue gave product **21** (540 mg, 65%).

For analytical purposes, compound **21** was per-*O*-acetylated under conventional conditions employing acetic anhydride in pyridine in the presence of 5 mol% of 4-dimethylaminopyridine. The sample of per-*O*-acetyl derivative **22** obtained *via* model

compound **20** exhibited $[\alpha]_D^{20}$ +14.9 (*c* 2.6, chloroform). The sucrose-derived material **22** had $[\alpha]_D^{20}$ +14.6 (*c* 3.7, chloroform) [A sample of compound **22**, prepared from commercially available compound **21** exhibited $[\alpha]_D^{20}$ +14.0 (*c* 2.6, chloroform)]: ^{1}H NMR ($CDCl_3$) δ 5.19 (m, 1 H, H-2), 4.29 (dd, 1 H, $J_{2,3}$ 3.8 Hz, $J_{3,3'}$ 11.9 Hz, H-3), 4.15 (dd, 1 H, $J_{2,3'}$ 6.3 Hz), 3.57 (d, 2 H, $J_{1,2}$ 5.1 Hz, H-1, H-1'); ^{13}C NMR δ 70.3, 68.1, 62.9.

Anal. Calcd for $C_{14}H_{18}O_5$ (266.29): C, 63.15; H, 6.81. Found: 62.85; H, 6.80 (from **20**). Found: C, 62.91; H, 7.06 (from **23**).

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