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Note

Decyl and dodecyl β-D-fructofuranosides

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Abstract

Decyl and dodecyl β-D-fructofuranosides are formed from D-fructose and catalysed by boron trifluoride alcoholates, in admixture with the corresponding α-D anomers and β-D-pyranosides. These were separated by chromatography and each of the products was fully characterized by NMR spectroscopy and as tetrakis(*p*-nitrobenzoates).

Keywords: Long-chain alkyl; Glycosidation; BF_3; Fructosides

1. Introduction

Decyl β-D-fructofuranoside (**1**) and dodecyl β-D-fructofuranoside (**2**) were required for comparison of various physical properties, among them, critical temperature and differential scanning calorimetry (DSC) measurements, with the corresponding, and previously described [1], β-D-glucofuranosides **3** and **4**. This was part of a programme investigating the relationship of structure to amphiphilic behaviour. A Japanese patent [2a] has suggested that long-chain alkyl or alkenyl D-fructofuranosides could have favourable properties in such personal care products as hair shampoos, but provides no synthetic details. An earlier related patent [2b] claimed the synthesis of some of these compounds directly from sucrose, but they were not specifically characterized, and no yields were quoted.

Although D-fructose is the second most abundant natural monosaccharide, its chemistry has not developed at the same rate as that of D-glucose, especially with respect to the formation of its glycosides [3,4]. The synthesis of specifically defined crystalline fructosides is rather difficult. Normal acid-catalysed glycosidation is temperamental and tends to lead to complex anomeric mixtures of furanosides and pyranosides, together with dehydration–degradation products, depending on the reaction temperature. Unlike aldosides, D-fructofuranosides and pyranosides are hydrolyzed at similar rates under acidic conditions, so that the overall control of ring size during reaction is difficult to achieve. Alternative routes based on Koenigs–Knorr-type procedures are also fraught with difficulties because of a lack of suitably protected, activated intermediates and complications arising from competitive orthoester formation [5]. An efficient procedure for the glycosidation of D-fructose, catalysed by elemental iodine, was described recently [4]. The reaction gave

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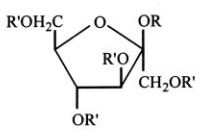
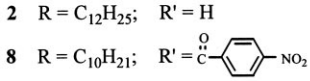
mainly fructofuranosides in high yields, but was found to be unsuitable for use with such higher alcohols as 1-octanol, and could not be employed for the current requirement. An earlier preliminary study [6,7] indicated that glycosidation of D-fructose with 1-octanol could be achieved using a number of simple homogeneous acid catalysts. With the stronger acids such as *p*-toluenesulfonic acid, pyranosidic products were favoured, but the yields decreased with increasing reaction times. Satisfactory yields of furanosides were claimed using oxalic acid as the catalyst. More recently [7] treatment of D-fructose with 1-dodecanol in the presence of anhydrous $FeCl_3$ in THF was shown to yield pyranosides (25%) almost exclusively.

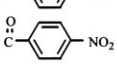
We describe the preparation of the desired furanosides **1** and **2**, together with their α-D-anomers **5** and **6**, which were obtained using a glycosidation–transglycosidation sequence induced by boron trifluoride–alcohol complexes. Reagents derived from boron trifluoride are not normally used in the direct glycosidation of unprotected reducing sugars, but are usually employed with sugar peresters. These reaction conditions are particularly useful for the synthesis of aryl glycosides [8] and 1-thioglycosides [9]. The direct glycosidation of *N*-acetyl-D-glucosamine and D-mannose using boron trifluoride etherate has been reported [6,10].

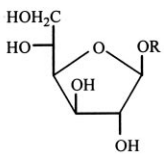


1 R = $C_{10}H_{21}$; R' = H

2 R = $C_{12}H_{25}$; R' = H



12 R = $C_{12}H_{25}$; 



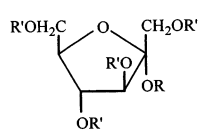
3 R = $C_{10}H_{21}$

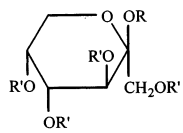
4 R = $C_{12}H_{25}$

The results of this current study, together with spectroscopic characterization and derivatization of the products, are now presented. During the course of this work an alternative method for the preparation of alkyl D-fructosides using heterogeneous silica–alumina cracking catalysts and acidic clays was described [11]. These conditions also yielded a preponderance of pyranosides. The isolation of compounds **2** and **6** by preparative HPLC was reported, but their identities were based solely on ^{13}C NMR spectroscopic data, and they were otherwise rather inadequately characterized.

2. Results and discussion

A suspension of D-fructose in EtOH was treated with a limited quantity of BF_3–MeOH complex (14%) and after ~18 h the presumed mixture of ethyl D-fructosides was treated with 1-decanol at 38–45 °C in vacuo. Column chromatography (9:1 CH_2Cl_2–MeOH) of the processed mixture gave the α-D-fructofuranoside **5**, followed by the known β-D-pyranoside **7** and the required β-D-fructofuranoside **1**. These were characterized as the corresponding *p*-nitrobenzoates **8**, **9**, and **10** by conventional treatment with *p*-nitrobenzoyl chloride–pyridine.

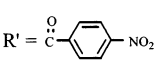


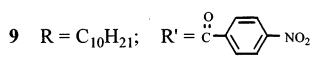


5 R = $C_{10}H_{21}$; R' = H

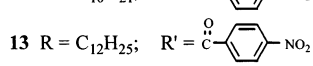
6 R = $C_{12}H_{25}$; R' = H

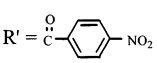
7 R = $C_{10}H_{21}$; R' = H

10 R = $C_{10}H_{21}$; 

9 R = $C_{10}H_{21}$; 

11 R = $C_{12}H_{25}$; R' = H

13 R = $C_{12}H_{25}$; 

14 R = $C_{12}H_{25}$; 

Treatment of D-fructose with 1-dodecanol in a similar manner was not successful because of precipitation of the intermediate mixture of ethyl D-fructosides. This problem was circumvented by treatment of D-fructose with 1-butanol in the presence of boron trifluoride–1-propanol complex at 55–60 °C for 8 h, followed by addition of 1-dodecanoland maintenance of this mixture in vacuo (1 mm) for 2 h at 50 °C. Under these conditions, the presumed intermediate 1-butyl fructosides remain in solution. Dodecyl β-D-fructopyranoside (**11**) was obtained by direct crystallization of a portion of the crude processed reaction mixture from EtOAc. Column

chromatography (9:1 CH_2Cl_2–MeOH) of the combined remaining residue and material obtained from the mother liquors yielded, sequentially, the α-D-fructofuranoside **6**, more of compound **11**, and the required compound **2**. These glycosides were also further characterized as the corresponding *p*-nitrobenzoates **12**, **13**, and **14**.

Compounds **8–10** and **12–14** could not be recrystallized in the usual fashion. No suitable solvents, or mixtures, could be found. In all those examples investigated the products were obtained as sticky, non-crystalline gums. They were purified by precipitation from their solutions in *N*,*N*-dimethylformamide by filtration into ice-cold brine solutions. These derivatives were obtained as amorphous solids which were analytically pure, but did not possess sharp melting points. They were characterized further by ^{1}H NMR spectroscopy (300 MHz).

Although the individual yields of some of the glycosides were quite low, the described procedures provided a route to the pure derivatives **1** and **2** sufficient in amount for determination of the necessary properties. The use of normal acid-catalysed glycosidation conditions (HCl, H_2SO_4) proved entirely unsuccessful for attainment of the required compounds.

3. Experimental

General methods.—Optical rotations were determined with a Perkin–Elmer automatic polarimeter, model 241 MC, at 20 °C on 1% solutions in the solvents indicated. Thin-layer chromatography (TLC) on pre-coated plates of silica gel (E. Merck) was performed using 2:1 hexane–EtOAc. Detection was effected by spraying with 3% H_2SO_4 in EtOH followed by heating at 140 °C. Column chromatography was performed on Silica Gel 60 (E. Merck) using 9:1 CH_2Cl_2–MeOH as eluent. ^{1}H NMR spectra were recorded on Bruker AM 300 (300 MHz) or 400 (400 MHz) spectrometers on solutions in $CDCl_3$ (internal standard Me_4Si) or D_2O. ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 100 MHz on solutions in $CDCl_3$ (internal Me_4Si) or D_2O (external 1,4-dioxane, 76.8 ppm).

Reaction of D-*fructose with 1-decanol.*—A stirred suspension of D-fructose (20.0 g, 0.11 mol) in EtOH (400 mL) was treated with a BF_3–MeOH complex (14% BF_3, 10 mL) and set aside overnight at room temperature. The mixture was then treated with 1-decanol (400 mL), maintained at 38–43 °C for 1.5 h in vacuo (19 mbar), cooled, treated with a mixture of ice-cold 5% aqueous K_2CO_3 (800 mL) and EtOAc (200 mL), stirred for 1.5 h and then set aside overnight at room temperature. The separated aq layer was extracted with EtOAc (300 mL) and the combined organic layers were washed with satd aq $NaHCO_3$ (2×200 mL), dried (Na_2SO_4), and concentrated in vacuo. Unreacted 1-decanol was distilled (~ 100 °C/0.01 mbar) from the residue and the crude material was then treated with *n*-hexane (500 mL) set aside at room temperature for 3 days, and the solvent then decanted to give a crude product (24.75 g, 70%). Column chromatography (20×9 cm) of a portion (18.20 g) of this material gave decyl α-D-fructofuranoside (**5**, 5.86 g, 22.5%) as a crystalline solid which was recrystallized from isopropyl ether to give pure **5** (3.39 g, 13%), mp 48–51 °C; clearing point (cp) 122.2–122.6 °C; $[\alpha]_D$ +41.3° ($CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 4.11 (d, 1 H, $J_{3,4}$ 5 Hz, H-3), 4.00 (t, 1 H, $J_{4,5}$ 6 Hz, H-4), 3.84 (m, 2 H), 3.70 (m, 3 H), 3.56 and 3.47 (2 m, each 2 H, OCH_2), 1.53 (m, 2 H, OCH_2 CH_2), 1.26 [m, 14 H, $O(CH_2)_2(CH_2)_7CH_3$], 0.88 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 107.8 (C-2), 83.0, 81.5, 76.7 (C-3, C-4, C-5), 61.8, 60.7, 60.5 [C-1, C-6 and $OCH_2(CH_2)_8CH_3$], 31.9, 30.1, 29.6, 29.5, 29.3, 26.1 ($2 \times$), 22.7 [OCH_2-$(CH_2)_8CH_3$], 14.1 (CH_3). Anal. Calc. for $C_{16}H_{32}O_6$ (320.425): C, 59.98, H, 10.07. Found: C, 59.55; H, 9.84.

Treatment of a portion (100 mg, 0.313 mmol) of pure **5** in dry pyridine (3 mL) with *p*-nitrobenzoyl chloride (290 mg, 156 mmol) in the conventional manner afforded crude **9** as solid material (0.264 g, 92%) for which no recrystallization solvent or solvent mixture was realized. A solution of the material in $HCONMe_2$ (6 mL) was filtered into a mixture of ice-water/satd aq NaCl

(1:1, 100 mL) with vigorous stirring. The resultant solid material was filtered, washed copiously with ice-cold water, and dried in vacuo (P_4O_{10}) to give **9** (0.217 g, 80%), mp 47.5–51 °C, $[\alpha]_D$ +25° ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (m, 16 H, aromatic H), 5.87 (d, 1 H, *J* 1 Hz, H-3), 5.47 (d, 1 H, *J* 4 Hz, H-4), 4.90 (m, 2 H, H-1a, H-6a), 4.75 (dd, 1 H, *J* 6 and 12 Hz, H-6b), 4.60 (m, 1 H, H-5), 4.51 (d, 1 H, *J* 12 Hz, H-1b), 3.70 [m, 2 H, $OCH_2(CH_2)_8CH_3$], 1.59 [m, 2 H, $OCH_2CH_2(CH_2)_7CH_3$], 1.37 [m, 2 H, $OCH_2CH_2(CH_2)_6CH_3$], 1.22 [m, 12H, $O(CH_2)_3(CH_2)_6CH_3$], 0.86 (t, 3 H, CH_3). Anal. Calc. for $C_{44}H_{44}N_4O_{18}$ (916.8476): C, 57.64; H, 4.84; N, 6.11. Found: C, 57.65; H, 4.85; N, 6.08.

Further elution gave material containing a mixture of glycosides (3.75 g) from which decyl β-D-fructopyranoside (**7**, 125 mg) crystallized, mp 131–133 °C (EtOAc), cp 125.5–126.5 °C, $[\alpha]_D$ −103.9° (4:1 CH_2Cl_2–MeOH); lit. [11] $[\alpha]_D$ −102.5° (EtOH). Treatment of this material (52.3 mg) in pyridine (3 mL) with *p*-nitrobenzoyl chloride (182 mg) followed by processing as already described gave the tetrakis(*p*-nitrobenzoate) **10** (116 mg, 97%), mp 60–68 °C; $[\alpha]_D$ −78.7° ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17–7.95 (m, 16 H, aromatic H), 6.22 (d, 1 H, *J* 10 Hz, H-3), 5.91 (dd, 1 H, *J* 10 and 3 Hz, H-4), 5.85 (m, 1 H, H-5), 4.94 (d, 1 H, *J* 12 Hz, H-1a), 4.39 (d, 1 H, *J* 12 Hz, H-1b), 4.20 (d, 1 H, *J* 13 Hz, H-6a), 4.12 (d, 1 H, *J* 13 Hz, H-6b), 3.81 and 3.70 (2 m, each 1 H, OCH_2), 1.78 [m, 2 H, $OCH_2CH_2(CH_2)_7CH_3$], 1.52–1.29 [m, 14 H, $O(CH_2)_2(CH_2)_7CH_3$], 0.89 (t, 3 H, CH_3). Anal. Calc. for $C_{44}H_{44}N_4O_{18}$ (916.8476): C, 57.64; H, 4.84; N, 6.11. Found: C, 57.19; H, 4.61; N, 6.17.

Continued elution then gave a third fraction (3.93 g), analysis (TLC) of which indicated that it contained the required **1** contaminated with other anomers.

Rechromatography (15 × 3.5 cm) of this material gave compound **1** (1.60 g) which on recrystallization (CH_2Cl_2–isopropylether) gave pure decyl β-D-fructofuranoside **1** (1.37 g, 3.7%), mp 57–59 °C; cp 138.5–139 °C; $[\alpha]_D$ −38.4° (4:1 CH_2Cl_2–MeOH); ^{1}H NMR (400 MHz, 38 °C, D_2O): δ 4.14 (d, 1 H, $J_{3,4}$ 8 Hz, H-3), 4.01 (t, 1 H, H-4), 3.85 (m, 1 H, H-5), 3.71 (m, 2 H), 3.59 (m, 3 H), 3.42 (m, 1 H), 1.51–1.27 [m, 18 H, $O(CH_2)_9CH_3$], 0.88 (t, 3 H, CH_3); ^{13}C NMR (38 °C, D_2O): δ 103.8 (C-2), 81.9, 77.6, 77.0 (C-3, C-4, and C-5), 64.3, 61.9, 60.8 [C-1, C-6 and $OCH_2(CH_2)_8CH_3$], 31.9, 30.2, 29.67, 29.63, 29.57, 29.3, 26.1, 22.6 [$OCH_2(CH_2)_8CH_3$], 14.1 (CH_3). Anal. Calc. for $C_{16}H_{32}O_6$ (320.425): C, 59.98; H, 10.07. Found: C, 59.94; H, 10.06.

Treatment of a portion (100.4 mg) of the above material in pyridine (3 mL) with *p*-nitrobenzoyl chloride (291 mg, 5 equiv.) as already described gave the tetra-ester **8** (191 mg, 66.5%), mp 49–56 °C, $[\alpha]_D$ −65° ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32–8.11 (m, 16 H, aromatic H), 6.00 (d, 1 H, *J* 6 Hz, H-3), 5.91 (m, 1 H, H-4), 4.85 (m, 1 H), 4.77 (d, 1 H, *J* 12 Hz, H-1), 4.66 (m, 3 H), 3.82–3.64 [2 m, each 1 H, $OCH_2(CH_2)_8CH_3$], 1.57 [m, 2 H, $OCH_2CH_2(CH_2)_7CH_3$], 1.23 [m, 14 H, $O(CH_2)_2(CH_2)_7CH_3$], 0.87 (t, 3 H, CH_3). Anal. Calc. for $C_{44}H_{44}N_4O_{18}$ (916.8476): C, 57.64; H, 4.84; N, 6.11. Found: C, 57.40; H, 4.65; N, 6.13.

Reaction of D-*fructose with 1-dodecanol.*— A stirred suspension of D-fructose (20 g, 0.11 mol) in 1-butanol (400 mL) was treated with a BF_3–1-propanol complex (14% BF_3, 10 mL) and maintained at 55–60 °C for 8 h. 1-Dodecanol (400 mL) was added to the mixture which was then held in vacuo (1.3 mbar) for 2 h at 50 °C. The cooled mixture was poured with stirring in ice cold 10% aq K_2CO_3 solution (700 mL), causing the precipitation of some 1-dodecanol, which was removed by filtration. The filtrate was treated with EtOAc (600 mL), set aside overnight at room temperature, the organic layer separated, and the aqueous layer extracted with more EtOAc (500 mL). The combined organic layers were washed sequentially with satd aq $NaHCO_3$ (2 × 500 mL), water (250 mL), dried (Na_2SO_4), concentrated in vacuo and the residue maintained at 120–130 °C (oil bath temperature) in vacuo (0.007 mbar) to remove excess 1-dodecanol. The resultant material was treated with hexane (600 mL), set aside for 1 h, the hexane decanted, the procedure repeated (2 ×), and the residue stored in vacuo to give the crude product (16.5 g, 43%). A portion of the crude product (8.07 g) was

crystallized from EtOAc, followed by aqueous EtOH to give pure dodecyl β-D-fructopyranoside (**11**, 1.62 g, 4.2%), mp 130.5–136 °C; cp 135.2–136 °C; $[\alpha]_D$ −95.6° (4:1 CH_2Cl_2–MeOH); lit. [11] $[\alpha]_D$ −82.5° (EtOH); ^{1}H NMR (400 MHz, $CDCl_3 + D_2O$, 58 °C): δ 3.96 (m, 2 H), 3.75 (m, 5 H), 3.47 [m, 2 H, $OCH_2(CH_2)_{10}CH_3$], 1.55 [m, 2 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.27 [m, 18 H, $OCH_2CH_2(CH_2)_9CH_3$], 0.88 (t, 3 H, CH_3); ^{13}C NMR (100 MHz, 58 °C): δ 100.4 (C-2), 71.1, 69.9, 69.6 (C-3, C-4 and C-5), 63.8, 62.8, 61.3 [C-1, C-6 and $OCH_2(CH_2)_{10}CH_3$], 31.9, 30.1, 29.6, 29.5, 29.3, 26.3, 22.6 [$OCH_2(CH_2)_{10}CH_3$], 14.0 (CH_3). Anal. Calc. for $C_{18}H_{36}O_6$ (348.47): C, 62.04; H, 10.41. Found C, 62.08; H, 10.40.

A boiling solution of the remainder of the crude product (8.44 g) in EtOH (75 mL) was treated with decolourizing charcoal, filtered, and the filtrate on cooling yielded a further quantity of **11** (2.74 g; 11.3%, see later) mp 132–135 °C; cp 134–137 °C; $[\alpha]_D$ −95.8° (4:1, CH_2Cl_2–MeOH).

Reaction of a portion of **11** (100 mg, 0.287 mmol) in pyridine (3 mL) with *p*-nitrobenzoyl chloride (267 mg, 1.44 mmol) as described yielded pure amorphous **14** (217 mg, 80%); mp 50–56 °C; $[\alpha]_D$ −173° ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16–7.95 (m, 16 H, aromatic H), 6.22 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.91 (dd, 1 H, $J_{4,5}$ 3 Hz, H-4), 5.85 (bs, 1 H, H-5), 4.94 (d, 1 H, $J_{1a,1b}$ 12 Hz, H-1a), 4.39 (d, 1 H, H-1b), 4.20 (bd, 1 H, $J_{6a,6b}$ 13 Hz, H-6a), 4.13 (bd, 1 H, H-6b), 3.81–3.70 (2 m, each 1 H, OCH_2), 1.78 [m, 2 H, OCH_2CH_2], 1.50 [m, 2 H, $O(CH_2)_2CH_2$], 1.42 [m, 2 H, $O(CH_2)_3CH_2$], 1.28 [m, 14 H, $O(CH_2)_4(CH_2)_7CH_3$], 0.88 (t, 3 H, CH_3). Anal. Calc. for $C_{46}H_{48}N_4O_{18}$ (944.90): C, 58.47; H, 5.12; N, 5.93. Found C, 58.54; H, 5.11; N, 5.97.

Column chromatography (20 × 9 cm) of the material (10.28 g), obtained by concentration in vacuo of the combined mother liquors from both of the foregoing crystallization processes, gave crystalline material (3.11 g) which on subsequent recrystallization from 1:1 ether–hexane, followed by isopropyl ether gave pure dodecyl α-D-fructofuranoside (**6**, 2.05 g, 5.3%), mp 55–57 °C; cp 137.5–138.5 °C; $[\alpha]_D$ +36.4° ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3 + D_2O$): δ 4.11 (d, 1 H, $J_{3,4}$ 4 Hz, H-3), 4.07 (m, 1 H, H-4), 3.93 (m, 1 H, H-5), 3.77 (m, 4 H, H-1a, H-1b, H-6a, H-6b), 3.58 and 3.49 (2 m, each 1 H, OCH_2), 1.54 [m, 2 H, OCH_2CH_2], 1.42–1.27 [m, 18 H, $OCH_2CH_2(CH_2)_9CH_3$], 0.88 (t, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 107.91 (C-2), 83.3, 81.4, 76.8 (C-3, C-4, C-5), 61.7, 60.8, 60.5 [C-1, C-6 and $OCH_2(CH_2)_{10}CH_3$], 31.9, 30.1, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7 [$OCH_2(CH_2)_{10}CH_3$], 14.1 (CH_3). Anal. Calc. for $C_{18}H_{36}O_6$ (348.4788): C, 62.04; H, 10.41. Found: C, 62.15; H, 10.40.

Compound **6** (102 mg) was treated as before with *p*-nitrobenzoyl chloride (277 mg) in pyridine (3 mL) to give **6** (187 mg, 68%), mp 43–50 °C; $[\alpha]_D$ +21.6° ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (m, 16 H, aromatic H), 5.88 (s, 1 H, H-3), 5.48 (d, 1 H, $J_{4,5}$ 4 Hz, H-4), 4.92 (d, 1 H, $J_{1a,1b}$ 12 Hz, H-1a), 4.88 (dd, 1 H, $J_{6a,6b}$ 12, $J_{6a,5}$ 4 Hz, H-6a), 4.75 (dd, 1 H, $J_{6b,5}$ 6 Hz, H-6b), 4.60 (m, 1 H, H-5), 4.52 (d, 1 H, H-1b), 3.71 (m, 2 H, OCH_2), 1.62 [m, 2 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.36 [m, 2 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$], 1.28 [m, 16 H, $O(CH_2)_3(CH_2)_8CH_3$], 0.87 (t, 3 H, CH_3). Anal. Calc. for $C_{46}H_{48}O_{18}N_4$ (944.9012): C, 58.47; H, 5.12; N, 5.93. Found C, 58.79; H, 5.21; N, 5.93.

Further elution gave an additional amount of compound **11** (1.09 g; total yield 14%), mp 130–132 °C (EtOAc); $[\alpha]_D$ −95.4° (4:1 CH_2Cl_2–MeOH), and continued elution then provided a third fraction (2.65 g) which on recrystallization (EtOAc) gave material (873 mg) containing two compounds. Partial concentration of the mother liquor and storage at 5 °C gave dodecyl β-D-fructofuranoside (**2**, 914 mg, 2.4%), mp 68.5–71 °C (CH_2Cl_2–isopropyl ether); cp 157–158 °C; $[\alpha]_D$ −30° (4:1 CH_2Cl_2–MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (d, 1 H, $J_{3,4}$ 8 Hz, H-3), 4.00 (t, 1 H, $J_{4,5}$ 8 Hz, H-4), 3.85 (m, 1 H, H-5), 3.71 (m, 2 H), 3.59 (m, 3 H), 3.42 (m, 1 H), 1.51 [m, 2 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.27 [m, 18 H, $OCH_2CH_2(CH_2)_9CH_3$], 0.88 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 103.8 (C-2), 81.9, 77.5, 77.0 (C-3, C-4, C-5), 64.3, 61.9, 60.8 [C-1, C-6 and $OCH_2(CH_2)_{10}CH_3$], 31.9, 30.2, 29.7, 29.3, 26.1, 22.6 [$OCH_2(CH_2)_{10}CH_3$], 14.0 (CH_3). Anal. Calc. for $C_{18}H_{36}O_6$ (348.4788): C, 62.04: H, 10.41. Found: C, 61.71: H, 10.33.

p-Nitrobenzoylation of compound **2** (102 mg) in the prescribed manner gave **12** (245 mg, 88%), mp 40–45 °C; $[\alpha]_D$ − 55.3° ($CDCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 8.21 (m, 16 H, aromatic H), 6.00 (d, 1 H, $J_{3,4}$ 6 Hz, H-3), 5.91 (m, 1 H, H-4), 4.86 (m, 1 H), 4.77 (d, 1 H, *J* 12 Hz, H-1), 4.67 (m, 3 H), 3.82 and 3.65 [2 m, each 1 H, $OCH_2(CH_2)_{10}CH_3$], 1.57 [m, 2 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.24 [m, 18 H, $O(CH_2)_2(CH_2)_9CH_3$], 0.88 (t, 3 H, CH_3). Anal. Calc. for $C_{46}H_{48}O_{18}N_4$ (944.9012): C, 58.47; H, 5.12; N, 5.93. Found: C, 58.79; H, 5.22; N, 5.97.

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