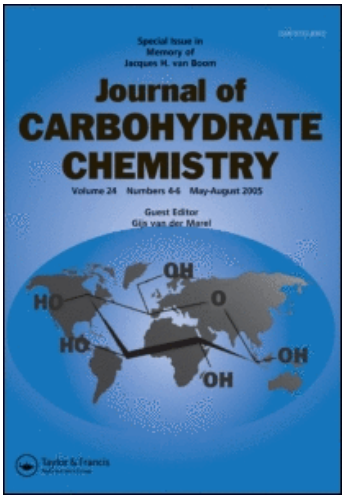

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Some Aspects of the Reaction of Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-Carbonate with 1-Dodecanol: Novel Non-Ionic Surfactants

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SOME ASPECTS OF THE REACTION OF METHYL 4,6-*O*-BENZYLIDENE-α-D-GLUCOPYRANOSIDE 2,3-CARBONATE WITH 1-DODECANOL: NOVEL NON-IONIC SURFACTANTS.

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ABSTRACT

The reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-cyclic carbonate (**2**) with 1-dodecanol in the presence of a catalytic amount of triethylamine to yield the 2-*O*- and the 3-*O*-alkoxycarbonyl esters **5** and **6** is described. Catalytic hydrogenation of **5** and **6** gave the deprotected mono-esters **3** and **4** which are of interest as potential non-ionic surfactants. The corresponding ethoxycarbonyl esters **7** and **8** were also prepared and their possible role as intermediates in the formation of **2** is discussed.

INTRODUCTION.

Various amphiphilic and mesogenic carbohydrate derivatives are attracting increasing attention. They include long-chain alkyl glycosides, their 1-thio-analogues, some 1,1-dithioacetals, alditol ethers, gluconamides, alkylidene-acetals, and long-chain fatty acid esters.[1]

Mono-*O*-acyl derivatives of methyl α-D-glucopyranoside (**1**) are useful[2] as emulsifiers in food processing as detergents, and in paints and varnishes. The selective esterification of **1** at the C-6 position using solvent-free base catalysed transesterification, or enzyme mediated processes has been described.[3,4] All of the positional isomers of methyl mono-*O*-tetradecanoyl-α-D-glucopyranoside have been prepared[5] using appropriate protecting group strategies. Compound **1** is inexpensive, commercially available in bulk, and may be considered as a potential hydrophilic "head-group" for sugar based non-ionic surfactants.

In other connections[6] we were interested in reactions of methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-cyclic carbonate (**2**). Compound **2** is known[7] to react *inter alia* with methanol and benzyl alcohol in the presence of triethylamine to give the corresponding 2-*O*- and 3-*O*-alkoxycarbonyl esters. The 2-esters were claimed to predominate. A simple route to methyl 2-*O*-dodecyloxycarbonyl-α-D-glucopyranoside (**3**) and the isomeric 3-ester **4** via the protected esters **5** and **6**, is described based on this approach. They are potential novel non-ionic surfactants. Long-chain mono-*O*-alkoxycarbonyl esters of **1** have not been described hitherto, due mainly to problems of selective substitution and non-commercial availability of the appropriate reagents. We have recently[8] demonstrated with mixed acyl and alkoxycarbonyl esters of sucrose, that the two types of ester groups exhibit approximately equivalent reactivities towards base hydrolysis.

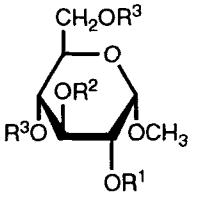
The preparation of the mono-*O*-ethoxycarbonyl esters **7** and **8** is also described, and their possible role as intermediates in the formation of the cyclic carbonate **2** discussed.

RESULTS AND DISCUSSION.

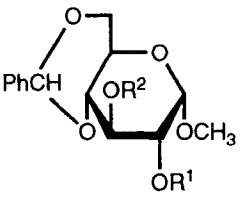
Reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**9**)[9,10] with an excess of ethyl chloroformate in the presence of triethylamine[11] gave compound **2** (81%). Compound **2** can be obtained in 98% yield by treatment of **9** with phosgene. The use of the less toxic ethyl chloroformate was considered more suitable for our purposes. Treatment of a solution of **2** in dichloromethane with dodecanol in the presence of a catalytic amount of triethylamine (10 mol %) yielded a mixture of the isomeric mono-esters **5** and **6** and unreacted **2** in the ratio 42 : 32 : 6.5 (HPLC), which was separated by column chromatography. No alcoholysis to the diol **9** appeared to occur under these reaction conditions. The product ratio was in general agreement with the results obtained earlier[7] for the base catalysed ring opening of **2** with methanol, which showed a preference for the formation of the C-2 ester.

Catalytic hydrogenolysis (Pd/C) of compounds **5** and **6** yielded **3** and **4** in essentially quantitative yields. Compound **3** was obtained crystalline whereas compound **4** was isolated as a syrup and characterised as its tris-*p*-nitrobenzoate **10**. The overall yields of **3** and **4** from the glucoside **1** were 30 and 20%, respectively.

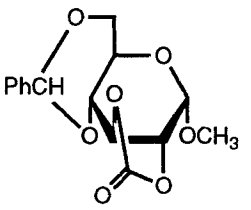
Compound **3** displayed interesting thermotropic liquid crystalline behaviour. The compound melted at 73-75 °C, but on supercooling a monotropic mesophase was observed. The mesophase could be classified tentatively as smectic A by its focal conic texture with oily streaks and pseudo-isotropic areas. This type of behaviour can be expected for surfactants with strong intermolecular hydrogen bonding[12] The monotropic mesophases are thermodynamically unstable and reversion to the more stable crystal structure will occur eventually.



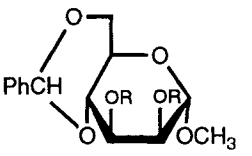
1 : $R^1 = R^2 = R^3 = H$
3 : $R^1 = -C(O)-OC_{12}H_{25}$, $R^2 = R^3 = H$
4 : $R^1 = R^3 = H$, $R^2 = -C(O)-OC_{12}H_{25}$
10 : $R^1 = R^3 = p\text{-}NO_2\text{-}Bz$, $R^2 = -C(O)-OC_{12}H_{25}$



5 : $R^1 = -C(O)-OC_{12}H_{25}$, $R^2 = H$
6 : $R^1 = H$, $R^2 = -C(O)-OC_{12}H_{25}$
7 : $R^1 = -C(O)-OEt$, $R^2 = H$
8 : $R^1 = H$, $R^2 = -C(O)-OEt$
9 : $R^1 = R^2 = H$
11: $R^1 = R^2 = -C(O)-OEt$



2



12: R = H
13: R = -O-C(O)-O

The procedure described here represents a convenient route to compounds **3** and **4** and offers scope for the preparation of several other analogues. These products could find application as novel non-ionic bio-detergents.[13]

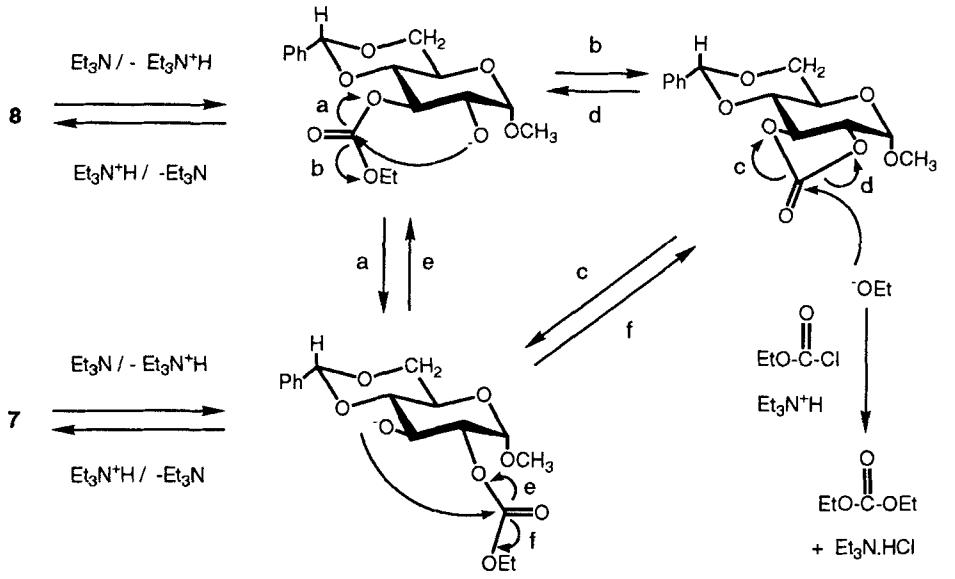
Treatment of **2** with ethanol - triethylamine yielded a mixture of the isomeric mono-ethoxycarbonyl derivatives **7** and **8** and the diol **9**, which was separated from the mixture by fractional crystallisation. Column chromatography of the residue provided pure **7** (21%) and **8** (28%). From these results it can be seen that extensive alcoholysis occurs under these conditions.

Although earlier work had suggested that treatment of either compound **7** or **8** with triethylamine did not yield the cyclic carbonate **2**, it is difficult to account for the formation of **2** from **9** without invoking ester **7** or **8** as intermediates. Mono-alkoxycarbonyl derivatives seem[14] to be involved when cyclic carbonates are produced from chloroformate esters in the presence of aqueous sodium hydroxide.

Dilute individual solutions of compounds **7** or **8** in dichloromethane treated with catalytic amounts of triethylamine and heated under reflux for 5 days contained mixtures of **7** and **8**, but no compound **2** was detected by TLC (ethyl acetate - hexane, 1:1). Analysis of the integrated signals assigned to the C-1 anomeric protons in the ^1H NMR spectra of compounds **7** and **8** occurring at 5.00 and 4.83 ppm, respectively, showed these

compounds to be present in an approximate ratio of 3:1 and 1:2, respectively, in the two mixtures. This was subsequently confirmed by HPLC analysis. The final equilibrium ratio of **7** and **8** by these transitions have not yet been determined.

SCHEME



The results suggest that **7** and **8** may possibly function as intermediates in the formation of **2** despite the earlier[7] negative assertion. Nucleophilic attack of an oxyanion, generated at the remaining free hydroxyl group by reaction with triethylamine, on the carbonyl carbon atom of the ester group could result in the intermediate formation of **2**. This would be immediately reopened by the ethoxide ions that are produced to give a mixture of **7** and **8**, which re-equilibrate in a similar manner. Under the usual[11] reaction conditions in the presence of a large excess of ethyl chloroformate, the ethoxide ions that are produced are effectively removed by reaction with the reagent to give diethyl carbonate, thereby shifting the equilibrium in favour of compound **2**. The alternative mechanism of ethoxycarbonyl ester migration (Scheme) may also be concurrent with the above proposed route. To the best of our knowledge there are no recorded examples of this type of transformation.

Reaction[11] of the diol **9** with ethyl chloroformate in the presence of pyridine yields only the diester **11**. Triethylamine, a stronger base, is required to promote the formation of **2** from **9**. Treatment of the mannoside **12**[6] with diethyl carbonate in the presence of a catalytic quantity of potassium carbonate and with continuous removal of ethanol produced, gives exclusively the *cisoid* cyclic carbonate **13**. This reaction must proceed

through a mono-ester intermediate with subsequent ring closure and provides additional evidence for the proposed pathway.

EXPERIMENTAL.

General procedures. Melting points were determined with a Reichert thermopan microscope and are uncorrected. Specific rotations were determined with a Perkin-Elmer 241 automatic polarimeter at 20 °C on 1% solutions in chloroform. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Chemical-ionisation (CI) mass spectra, induced with methane gas at 200 °C and emission current 0.5 mAmp, were determined on a VG 7070E spectrometer. ^{1}H NMR spectra were recorded with a Varian EM 390 (90 MHz) or Bruker AM 400 (400 MHz, FT) spectrometer on solutions in $CDCl_3$ (internal standard Me_4Si). Column chromatography was performed on Silica Gel 60 with the solvent mixtures indicated. TLC was performed on pre-coated plates of silica gel (Merck) in the solvent mixures indicated and detection by charring with 5% H_2SO_4 in ethanol at 140 °C. HPLC was performed on a column (250 x 4.6 mm) of Silica Gel 60 (5 μm) with hexane - ethyl acetate (3 : 2) as the eluent at a flow rate of 1 mL / min using a spectra physics 8700 solvent delivery system. Detection was achieved using a Spectra Physics 8400 variable wavelength UV / VIS detector unit operating at 254 nm and coupled to a Spectra Physics 4100 computing integrator. Evaporations were conducted *in vacuo*.

Methyl 4,6-*O*-Benzylidene-2-*O*-dodecyloxycarbonyl-α-D-glucopyranoside (5) And Methyl 4,6-*O*-Benzylidene-3-*O*-dodecyloxycarbonyl-α-D-glucopyranoside (6). A stirred solution of compound **2**[11] (10 g, 32.5 mmol) in dichloromethane (30 mL) containing dodecanol (18.6 g, 0.1 mol) was treated with triethylamine (0.5 mL, 10 mol %) and then set aside at room temperature for 16 h. The mixture was concentrated *in vacuo* and the excess dodecanol removed from the residue by molecular distillation (120 °C, / 0.6 mmHg). Column chromatography (hexane-ethyl acetate, 3:1) of the residue (17.3 g) yielded **5** (5.26 g, 33%): mp 75-77 °C (from hexane), $[\alpha]_D$ +67.5°; IR (KBr) 3460 (OH), 1745, 1290 and 1245 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 7.50-7.25 (m, 5H, arom. H), 5.55 (s, 1H, $C_6H_5C\underline{H}$), 5.00 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.65 (d.d., 1H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 9.7 Hz, H-2), 4.31 (dd, 1H,$J_{5,6e}$ = 4.6 Hz, $J_{6e,6a}$ = 10.2 Hz, H-6e), 4.22 (d.d.d, 1H, $J_{3,OH}$ = 2.5 Hz, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 4.16 (t, 2H, J = 6.8 Hz, $OC\underline{H}_2$-$C_{11}H_{23}$), 3.84 (ddd, 1H, $J_{4,5}$ = $J_{5,6a}$ = 9.4 Hz, $J_{5,6e}$ = 4.6 Hz, H-5), 3.76 (dd, 1H, $J_{5,6a}$ = 9.4 Hz $J_{6e,6a}$ = 10.2 Hz, H-6a), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 3.42 (s, 3H, $OC\underline{H}_3$), 2.78 (d., 1H, $J_{3,OH}$ = 2.5 Hz, C-3-O$\underline{H}$), 1.70 (m, 2H, OCH_2-$C\underline{H}_2$-$C_{10}H_{21}$), 1.25 (m, 18H, OCH_2-CH_2-$(C\underline{H}_2)_9$-CH_3), 0.88 (t, 3H, J = 6.7 Hz O-$(CH_2)_{11}$-$C\underline{H}_3$) ppm; ^{13}C NMR ($CDCl_3$) δ 154.8 (C=O),

136.9, 129.2, 128.3, 126.3 (arom. C), 101.96 ($C_6H_5\underline{C}H$), 97.5 (C-1), 81.3, 76.6, 68.6, and 62.0 (C-2 to C-5), 68.8 (C-6 and $O\underline{C}H_2C_{11}H_{23}$), 55.3 ($O\underline{C}H_3$) 31.8, 29.5, 29.4, 29.3, 29.2, 28.5, 25.6, 22.6 ($\underline{C}H_2$ alkyl chain), 14.0 ($\underline{C}H_3$, alkyl chain) ppm; M/e 495 ($M^+ + 1$), 463 ($M^+ + 1- CH_3OH$), 309 ($M^+ + 1- C_{12}H_{25}OH$), 283 ($M^+ + 1- C_{12}H_{25}OH - C_2H_2$), 265 ($M^+ + 1- C_{12}H_{25}OCO_2H$), 107 ($^+C_7H_7O$), 91 ($^+C_7H_7$), 77 ($^+C_6H_5$).

Anal. Calcd for $C_{27}H_{42}O_8$ (494.628): C, 65.56; H, 8.56. Found: C, 65.27; H, 8.49%.

Further elution gave **6** (5.41 g, 34%): mp 64 - 67 °C (from hexane), $[\alpha]_D$ +69.3°; IR (KBr) 3460 (OH), 1745 and 1270 cm^{-1} (ester); ^1H NMR ($CDCl_3$) δ 7.46-7.25 (m, 5H, $C_6\underline{H}_5$), 5.49 (s, 1H, $C_6H_5C\underline{H}$), 5.11 (t, 1H, $J_{3,4} = J_{2,3} = 9.6$ Hz, H-3), 4.80 (d, 1H, $J_{1,2} = 3.8$ Hz, H-1), 4.30 (d.d, 1H, $J_{6e,6a} = 10.2$ Hz, $J_{5,6e} = 4.7$ Hz, H-6e), 4.14 (t, 2H, J = 6.8 Hz, $OC\underline{H}_2$-$C_{11}H_{23}$), 3.88 (d.d.d., 1H, $J_{5,6e} = 4.8$ Hz $J_{5,6a} = 10.2$ Hz, $J_{4,5} = 9.6$ Hz, H-5), 3.75 (t, 1H, $J_{6a,6e} = J_{6a,5} = 10.2$ Hz, H-6a), 3.72 (ddd, 1H, $J_{1,2} = 3.8$ Hz, $J_{2,3} = 9.6$ Hz, $J_{2,0H} = 11.3$ Hz, H-2), 3.62 (t, 1H, $J_{4,5} = J_{3,4} = 9.6$ Hz, H-4), 3.47 (s, 3H, $OC\underline{H}_3$), 2.39 (d., 1H, C-2-O$\underline{H}$, $J_{2,OH} = 11.3$ Hz), 1.65 (m, 2H $OCH_2C\underline{H}_2C_{10}H_{21}$), 1.24 (m, 18H, $OCH_2CH_2(C\underline{H}_2)_9CH_3$), 0.88 (t, 3H, J = 6.6 Hz, $O(CH_2)_{11}C\underline{H}_3$); ^{13}C NMR ($CDCl_3$): δ 155.2 (C=O), 136.9, 129.0, 128.1 and 126.1 (arom. C), 101.4 ($C_6H_5\underline{C}H$), 100.0 (C-1), 78.5, 76.2, 71.6 and 62.6 (C-2 to C-5), 68.8 and 68.5 (C-6 and $O\underline{C}H_2C_{11}H_{23}$), 55.5 ($OCH_3$), 31.8, 29.5, 29.4, 29.3, 29.1, 28.5, 25.6 and22.6 ($OCH_2(\underline{C}H_2)_{10}CH_3$), 14.0 ($O(CH_2)_{11}\underline{C}H_3$) ppm; M/e 495 ($M^+ + 1$), 463 ($M^+ + 1- CH_3OH$), 309 ($M^+ + 1- C_{12}H_{25}OH$), 283 ($M^+ + 1- C_{12}H_{25}OH - C_2H_2$), 265 ($M^+ + 1- C_{12}H_{25}OCO_2H$), 107 ($^+C_7H_7O$), 91 ($^+C_7H_7$), 77 ($^+C_6H_5$).

Anal. Calcd for $C_{27}H_{42}O_8$ (494.628): C, 65.56; H, 8.56. Found: C, 65.20; H, 8.43%.

Methyl 2-*O*-Dodecyloxycarbonyl-α-D-glucopyranoside (3). A solution of compound **5** (6.0 g, 12.1 mmol) in methanol (100 mL) was hydrogenated (1 atm) in the presence of palladised charcoal (10%, 150 mg) for 3 h when hydrogen uptake ceased. The catalyst was removed by filtration, washed with methanol, and the combined filtrate and washings concentrated *in vacuo*. The syrupy residue crystallised on storage and was recrystallised (ether - hexane) to give **3** (4.76 g, 97%): mp 73-75°C; clearing point 46-48°C; $[\alpha]_D$ +90°; ^1H NMR ($CDCl_3$ / D_2O) δ 4.94 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1), 4.55 (dd, 1H, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 9.9$ Hz, H-2), 4.14 (m, 2H, $OC\underline{H}_2$-$C_{11}H_{23}$), 3.92 (t, 1H, $J_{3,4} = J_{2,3} = 9.9$ Hz, H-3), 3.88 (dd, 1H, $J_{6a,6b} = -12.1$ Hz, $J_{5,6a} = 3.0$ Hz, H-6a), 3.81 (dd, 1H, $J_{5,6b} = 2.4$ Hz, $J_{5,6a} = 3.0$ Hz, H-6b), 3.66 (t, 1H,, $J_{4,5} = J_{3,4} = 9.9$ Hz, H-4), 3.59 (m, 1H, H-5), 3.38 (s, 3H, OCH_3), 1.67 (m, 2H, $OCH_2C\underline{H}_2C_{10}H_{21}$), 1.26 (m, 18H, OCH_2CH_2-$(C\underline{H}_2)_9$-CH_3), 0.88 (t, J = 6.5 Hz, 3H, O-$(CH_2)_{11}$-$C\underline{H}_3$) ppm; ^{13}C NMR δ 154.97 (C=O), 96.98 (C-1), 68.72 (C-6), 76.24, 71.37, 71.01 and 69.68 (C-2 to C-5),

61.12 ($O\underline{C}H_2$-$C_{11}H_{23}$), 55.16 ($O\underline{C}H_3$), 31.85 , 29.58, 29.27, 28.48, 25.61 and 22.63 (aliph. $\underline{C}H_2$), 14.05 (O-$(CH_2)_{11}$-$\underline{C}H_3$) ppm. M/e 407 (M^+ + 1), 375 (M^+ + 1 - CH_3OH), 357 (M^+ + 1 - CH_3OH - H_2O), 221 (M^+ + 1 - $C_{12}H_{25}OH$), 169 ($^+C_{12}H_{25}$).

Anal. Calcd for $C_{20}H_{38}O_8$ (406.518): C, 59.1; H, 9.42. Found: C, 59.13; H, 9.33%.

Methyl 3-*O*-Dodecyloxycarbonyl-α-D-glucopyranoside (4). Reduction of **6** (2 g, 4 mmol) in the same manner as described for compound **5** yielded pure (TLC, ethyl acetate - hexane; 1:3) **4** as a syrup (1.62 g, 98%), $[\alpha]_D$ +98.7°; ^{1}H NMR ($CDCl_3$) δ 4.79 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.88 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3) 4.14 (m, 2H, unresolved), 3.85 (br s, 2H, one OH and an unresolved signal), 3.68- 3.57 (m, 4H, unresolved), 3.45 (s, 3H, $O\underline{C}H_3$), 2.67 (br s, 1H, OH), 2.62 (br d, 1H, J = 10.5 Hz, OH), 1.69 (m, 2H, OCH_2-$C\underline{H}_2$-$C_{10}H_{21}$), 1.25 (m, 18H, OCH_2-CH_2-$(C\underline{H}_2)_9$-CH_3), 0.88 (t, 3H, J = 6.8 Hz, O-$(CH_2)_{11}$-CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ 156.20 (C=O), 99.41 (C-1), 68.83 (C-6), 61.68 (O-$\underline{C}H_2$-$C_{11}H_{23}$), 55.39 ($O\underline{C}H_3$), 80.21, 71.30, 70.75 and 68.50 (C-2 to C-5), 31.84, 29.55, 29.45, 29.27, 29.20, 28.50, 25.60 and 22.61 (O-CH_2-$(\underline{C}H_2)_{10}$-CH_3), 14.04 (O-$(CH_2)_{11}$-$\underline{C}H_3$) ppm; M/e 407 (M^+ + 1), 375 (M^+ + 1 - CH_3OH), 357 (M^+ + 1 - CH_3OH - H_2O), 221 (M^+ + 1 - $C_{12}H_{25}OH$), 169 ($^+C_{12}H_{25}$).

MS (peak match): Calcd for $(M + H)^+$, $C_{20}H_{39}O_8$: 407.2645 amu. Found 407.26455 ± 0.00081 amu.

Methyl 3-*O*-Dodecyloxycarbonyl-α-D-glucopyranoside 2,4,6 tris-*p*-nitrobenzoate (10). A solution of compound **4** (0.53 g, 1.31 mmol) in pyridine (10 mL) was treated with *p*-nitrobenzoyl chloride (0.8 g, 4.3 mmol) and set aside at room temperature for 16 h. The mixture was processed in the usual manner. Column chromatography (hexane - ethyl acetate) of the crude product (0.95 g, 85%) gave a syrup (0.69 g) which was dissolved in *N,N*-dimethylformamide (5 mL) and then reprecipitated by pouring into ice-water to give pure **10** (0.6 g, 54%): mp 46-49 °C; $[\alpha]_D$ +91.8°; ^{1}H NMR ($CDCl_3$) δ 8.20-8.32 (m, 12H, arom. H), 5.77 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-3 [15]), 5.28 (dd, 1H,$J_{3,4}$ = 9.8 Hz, $J_{4,5}$ = 9.8 Hz, H-4[15]), 5.25 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.20 (dd, 1H, H-2), 4.66 (dd, 1H, $J_{6a,6b}$ = -12.4 Hz, $J_{5,6a}$ = 2.2 Hz, H-6a), 4.50 (dd, 1H, $J_{5,6b}$ = 4.5 Hz,1H, $J_{6a,6b}$ = -12.4 Hz, H-6b), 4.39 (m, 1H, H-5), 3.94 (m, 2H, O-$C\underline{H}_2$-$C_{11}H_{23}$), 3.48 (s, 3H, $O\underline{C}H_3$), 1.36-1.03 (m, 20H, O-CH_2-$(C\underline{H}_2)_{10}$-CH_3), 0.87 (t, 3H, J = 6.7 Hz, O-$(CH_2)_{11}$-$C\underline{H}_3$ ppm; ^{13}C NMR δ 164.24, 163.68, 163.36 (C=O *p*-nitrobenzoate), 154.68 (C=O carbonate ester), 150.92, 150.72, 134.82, 134.2, 133.93, 131.10, 130.83 and 123.66 (arom. C), 96.59 (C-1), 73.48, 72.29, 69.91 and 67.17 (C2 to C-5), 68.89 and 63.09 (C-6 and O-$\underline{C}H_2$-$C_{11}H_{23}$), 55.82 ($O\underline{C}H_3$), 31.83, 29.51, 29.41, 29.28, 28.97, 28.30, 25.30 and 22.62, (O-CH_2-$(\underline{C}H_2)_{10}$-CH_3), 14.06 (O-

($(CH_2)_{11}$-$\underline{C}H_3$) ppm; M/e 852 (M^+ - H), 822 (M^+ - OCH_3), 687 (M^+ - *p*-NO_2-C_6H_4-C(O)-O), 160 (*p*-NO_2-C_6H_4-C(O)-O^+), 150 (*p*-NO_2-C_6H_4-C^+=O).

Anal. Calcd. for $C_{41}H_{47}N_3O_{17}$ (853.863): C, 57.68; H, 5.55. Found: C, 57.76; H, 4.89%.

Methyl 4,6-*O*-Benzylidene-2-*O*-ethoxycarbonyl-α-D-glucopyranoside (7) And Methyl 4,6-*O*-Benzylidene-3-*O*-ethoxycarbonyl-α-D-glucopyranoside (8). A stirred solution of compound **2**[11] (5.0 g, 16.2 mmol) in ethanol (50 mL) containing a catalytic quantity of triethylamine (0.2 mL, 1.6 mmol) was heated under reflux for 24 h. The mixture was concentrated *in vacuo* and the residue (5.19 g) dissolved in hexane - ethyl acetate (2:1, 30 mL) to give crystalline **9** (2.17 g, 47%), mp 163-165 °C; lit.[9] mp 164-165 °C.

The filtrate was concentrated *in vacuo* and column chromatography (hexane - ethyl acetate, 2:1) of the residue gave compound **7** (1.2 g, 21%): mp 100-103 °C; $[\alpha]_D$ +95°, lit.: mp 100-101 °C; $[\alpha]_D$ +96°; ^1H NMR ($CDCl_3$ / D_2O) δ 7.51-7.34 (m, 5H, arom. H), 5.56 (s, 1H, $C_6H_5C\underline{H}$), 5.00 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.65 (d.d., 1H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.29 (d.d, 1H,$J_{5,6e}$ = 4.4 Hz, $J_{6e,6a}$ = 9.8 Hz, H-6e), 4.20 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 4.17 (q, 2H, J = 6.8 Hz, $OC\underline{H}_2CH_3$), 3.84 (ddd, 1H, $J_{4,5}$ = $J_{5,6a}$ = 9.6 Hz, $J_{5,6e}$ = 4.4 Hz, H-5), 3.78 (dd, 1H, $J_{5,6a}$ = 9.4 Hz $J_{6e,6a}$ = 9.8 Hz, H-6a), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.42 (s, 3H, $OC\underline{H}_3$),1.43 (t, 3H, J = 7.2 Hz, $OCH_2C\underline{H}_3$) ppm.

Further elution gave compound **8** (1.59 g, 28%): mp 142-144 °C; $[\alpha]_D$ +99°; lit.[11]: mp 143-144 °C; $[\alpha]_D$ +101°; ^1H NMR ($CDCl_3$ / D_2O) δ 7.51-7.34 (m, 5H, $C_6\underline{H}_5$), 5.55 (s, 1H, $C_6H_5C\underline{H}$), 5.10 (t, 1H, $J_{3,4}$ = J2,3 = 9.6 Hz, H-3), 4.83 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.31 (dd, 1H, $J_{6e,6a}$ = 10.2 Hz, $J_{5,6e}$ = 4.7 Hz, H-6e), 4.19 (q, 2H, J = 7.2 Hz, $OC\underline{H}_2CH_3$), 3.84 (ddd, 1H, $J_{5,6e}$ = 4.8 Hz $J_{5,6a}$ = 10.2 Hz, $J_{4,5}$ = 9.6 Hz, H-5), 3.77 (t, 1H, $J_{6a,6e}$ = $J_{6a,5}$ = 10.2 Hz, H-6a), 3.75 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 3.62 (t, 1H, $J_{4,5}$ = $J_{3,4}$ = 9.6 Hz, H-4), 3.47 (s, 3H, $OC\underline{H}_3$), 1.33 (t, 3H, J = 7.2 Hz, $OCH_2C\underline{H}_3$) ppm.

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