J Wood Sci (2004) 50:248–252
DOI 10.1007/s10086-003-0545-7

ORIGINAL ARTICLE

Shinsuke Ifuku · Hiroshi Kamitakahara
Fumiaki Nakatsubo

Preparation of novel reagents 4-alkoxytrityl chlorides and their reaction with methyl α-D-glucoside

Received: February 20, 2003 / Accepted: May 16, 2003

Abstract A series of novel 4-*O*-alkoxytrityl chlorides (**1**) with different chain lengths was synthesized as a novel reagent for obtaining 6-*O*-alkylated cellulose with high regioselectivity via trityl groups in one reaction step without the use of any protective groups. These chlorides were reacted with methyl α-D-glucoside, which was used as a model compound, to examine the reactivities toward the primary hydroxyl groups of cellulose to afford a series of 6-*O*-alkylated methyl α-D-glucosides in high yields. The product compounds were found to have interesting solubilities and thermal properties. Thus, newly prepared trityl chloride derivatives were found to be useful regioselective derivatization reagents on the primary hydroxyl group in carbohydrates, especially in cellulose.

Key words 4-Alkoxytrityl chloride · Methyl 6-*O*-(4-alkoxytrityl)-α-D-glucoside · Regioselective 6-*O*-alkylation · 6-*O*-Alkylated cellulose

Introduction

Cellulose is, at present, widely used as fibers[1] and films[2] produced from regenerated cellulose, and versatile cellulose derivatives modified mainly by esterification[3] and etherification.[4] However, for the molecular design of future advanced polymeric materials having special functions, it is very important to establish a method for preparing cellulose derivatives that are substituted with high regiselectivity to give well-defined structures. In particular, derivatization at the primary hydroxyl group is fairly easy and is of great utility from this viewpoint.

S. Ifuku · H. Kamitakahara · F. Nakatsubo (✉)
Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan
Tel. +81-75-753-6256; Fax +81-75-753-6300
e-mail: tsubosan@kais.kyoto-u.ac.jp

Trityl chloride, having high selectivity for primary hydroxyl groups,[5–7] is used as a protective group for preparing cellulose derivatives with high regioselectivity.[8] However, the synthetic route for these derivatives needs two additional reactions for the introduction and removal of the protective group.[9,10] Additional reaction steps are implicated in various detrimental effects such as decrease of regioselectivity and loss of degree of polymerizaion due to the β glucosidic bond cleavage, as well as limited reproducibility and insufficient yields. Hence, methods for regioselective derivatization without the use of protective groups are important, especially for cellulose derivatization. In such chemistry, if trityl chloride derivatives bearing special functional groups were used, the cellulose derivatives with the special functional groups attached may be obtained in a one-step reaction without introduction and removal of the protective group. However, there is no report of such work to date.

Generally, when nonpolar and hydrophobic long-chain alkyl groups are introduced into polar hydrophilic carbohydrate molecules, the resultant alkylated carbohydrates are expected to have improved solubilities and meltabilities.[11,12] Such properties may enable further chemical modifications in organic solvents or fusion molding in the case of polysaccharides.

Herein we report the preparation of a series of novel 4-*O*-alkoxytrityl chlorides with different chain lengths, reactions with methyl α-D-glucopyranoside as a model compound to examine reactivities with the primary hydroxyl groups in wood-related polyhexosans such as cellulose, and several properties of the products.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded with a Varian Inova 300 FT NMR instrument (300 MHz) in chloroform-*d* with tetramethylsilane (Me_4Si) as the internal standard, or in

Me_2SO-d_6. Chemical shifts (δ) and coupling constants (J) were given in ppm and Hz, respectively. Optical rotations were measured at 25°C using a Jasco Dip-1000 digital polarimeter. Thin layer chlomatography (TLC) was performed on Merck Kieselgel 60 F_{254} (E. Merck) glass plates.

Methyl 4-benzyloxybenzoate (**3**)

Compound **2** (25 g, 164 mmol) was dissolved in DMF (350 ml) containing BnBr (29.3 ml, 248 mmol) and ground K_2CO_3 (45.3 g, 328 mmol). The reaction mixture was heated at 60°C overnight. Methanol (MeOH) was added to the reaction mixture to decompose excess BnBr. After cooling, the reaction mixture was filtered and the residue was washed with ethyl acetate (EtOAc). The combined filtrate and washings were concentrated in vacuo. The residue was dissolved in EtOAc, and the solution was washed with brine, dried over Na_2SO_4, and concentrated. The residue was recrystallized from *n*-hexane to yield compound **3** as colorless crystals (39.3 g, 99%): mp 98°–99°C; ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 3H, CH_3), 5.12 (s, 2H, CH_2), 6.98–8.01 (m, 9H, Ar); Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.35; H, 5.88.

4-Benzyloxytrityl alcohol (**6**) by route **A**

In a 1-liter two-necked flask fitted with a dropping funnel and reflux condenser, a 3 M solution of PhMgBr in diethyl ether (Et_2O) (92.4 ml, 277 mmol, Tokyo Kasei Kogyo) and anhydrous Et_2O (100 ml) were added. To the stirred solution, compound **3** (30.5 g, 126 mmol) in anhydrous benzene (176 ml) was added dropwise at such a rate that the mixture refluxed gently. The flask was cooled in a water bath during the addition, which required 1 h. After the addition was complete, the mixture was refluxed for 1 h. The reaction mixture was cooled in an ice–salt bath and then poured slowly, with constant stirring, into a mixture of 370 g of cracked ice and 12 ml of concentrated H_2SO_4. The mixture was stirred at intervals until all the solid that separated at the benzene–water interface had dissolved. The organic layer was separated and washed successively with water, 5% solution of $NaHCO_3$, and finally with water. The solution was dried over Na_2SO_4 and concentrated. The residue was recrystallized from *n*-hexane to yield compound **6** as colorless crystals (32.8 g, 71%): mp 97°–99°C; ^{1}H NMR ($CDCl_3$): δ 5.05 (s, 2H, CH_2), 6.89–7.41 (m, 19H, Ar); Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.06; H, 6.02.

4-Benzyloxybenzophenone (**5**)

Compound **5** was obtained from compound **4** (50 g, 252 mmol) in the same manner as that for the preparation of compound **3**. Compound **5** was purified by recrystallization from *n*-hexane to yield colorless crystals (71.8 g, 99%): mp 82°–84°C; ^{1}H NMR ($CDCl_3$): δ 5.14 (s, 2H, CH_2), 7.02–7.84 (m, 14H, Ar); Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.12; H, 5.82.

4-Benzyloxytrityl alcohol (**6**) by route **B**

Compound **6** was obtained from compound **5** (73.8 g, 256 mmol) and 3 M solution of PhMgBr in Et_2O (83 ml, 256 mmol) in the same manner as that for the preparation of compound **6** from compound **3** (88.4 g, 94%).

4-Hydroxytrityl alcohol (**7**)

Compound **6** (19 g, 51.8 mmol) was dissolved in EtOAc (200 ml) and 10% Pd–C (6 g) was added. The reaction mixture was stirred under hydrogen gas overnight at room temperature. The Pd–C was filtered off and the residue washed with EtOAc. The combined filtrate and washings were concentrated in vacuo to give crude crystals that were recrystallized from *n*-hexane to yield compound **7** as yellow powder (13.6 g, 95%): mp 139°–141°C; ^{1}H NMR (Me_2SO-d_6): δ 6.63–7.30 (m, 14H, Ar); Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.51; H, 5.81.

4-Alkoxytrityl alcohol (**8**)

Solutions of compound **7** (2 g, 7.23 mmol) and *n*-alkyl Br ($C_nH_{2n+1}Br$; n = 4, 12, 18; 8.68 mmol) in DMF (25 ml) were treated with ground K_2CO_3 (2 g, 14.5 mmol), and the resulting mixtures were heated at 60°C overnight. After cooling, the mixtures were filtered and the residues washed with EtOAc. The combined filtrate and washings for each reaction were concentrated in vacuo. The residues were dissolved in EtOAc, and the organic solutions were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residues were recrystallized from *n*-hexane to yield compound series **8** as colorless crystals (99%):

Data for n = 4: mp 67°–69°C; ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, $J_{\omega,\omega-1}$ 7.5 Hz, ω-CH_3), 1.48 (m, 2H, CH_2CH_3), 1.76 (m, 2H, $CH_2C_2H_5$), 3.95 (t, 2H, $J_{\alpha,\beta}$ 6.3 Hz, α-CH_2), 6.81–7.34 (m, 14H, Ar); Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.96; H, 7.55.

Data for n = 12: mp 52°–54°C; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J_{\omega,\omega-1}$ 6.9 Hz, ω-CH_3), 1.26–1.77 (m, 20H, $(CH_2)_{10}CH_3$), 3.93 (t, 2H, $J_{\alpha,\beta}$ 6.6 Hz, α-CH_2), 6.81–7.31 (m, 14H, Ar); Anal. Calcd. for $C_{31}H_{39}O_2$: C, 83.74; H, 9.07. Found: C, 83.44; H, 8.98.

Data for n = 18: mp 65°–67°C; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J_{\omega,\omega-1}$ 6.9 Hz, ω-CH_3), 1.26–1.79 (m, 32H, $(CH_2)_{16}CH_3$), 3.93 (t, 2H, $J_{\alpha,\beta}$ 6.3 Hz, α-CH_2), 6.81–7.35 (m, 14H, Ar); Anal. Calcd. for $C_{37}H_{52}O_2$: C, 84.04; H, 9.91. Found: C, 84.01; H, 10.02.

4-Alkoxytrityl chloride (**1**)

A mixture of series compound **8** (3.00 mmol) and dry benzene (0.5 ml) was placed in a 10-ml flask with a reflux condenser. The mixture was heated at 60°C and AcCl (1 ml) was added through the top of the condenser. Refluxing was continued for 1 h before the solution was cooled to room temperature and concentrated in vacuo. The residue was

recrystallized from dry *n*-hexane to yield compound **1** as a colourless crystal ($n = 4$) and solids ($n = 12, 18$) (95%):

Data for $n = 4$: mp 83°–85°C; ^{1}H NMR ($CDCl_3$): δ 0.97 (t, 3H, $J_{\omega,\omega-1}$ 7.2 Hz, ω-CH_3), 1.49 (m, 2H, -CH_2CH$_3$), 1.76 (m, 2H, CH_2C$_2$H$_5$), 3.96 (t, 2H, $J_{\alpha,\beta}$ 6.6 Hz, α-CH_2), 6.79–7.31 (m, 14H, Ar); Anal. Calcd. for $C_{23}H_{23}ClO$: C, 78.73; H, 6.61; Cl, 10.10. Found: C, 78.93; H, 6.35; Cl, 10.04.

Data for $n = 12$: mp 29°–31°C; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J_{\omega,\omega-1}$ 6.9 Hz, ω-CH_3), 1.26–1.80 (m, 20H, (CH_2)$_{10}$CH$_3$), 3.94 (t, 2H, $J_{\alpha,\beta}$ 6.3 Hz, α-CH_2), 6.79–7.32 (m, 14H, Ar); Anal. Calcd. for $C_{31}H_{39}ClO$: C, 80.40; H, 8.49; Cl, 7.66. Found: C, 80.59; H, 8.54; Cl, 7.49.

Data for $n = 18$: mp 47°–49°C; ^{1}H NMR ($CDCl_3$):_δ 0.88 (t, 3H, $J_{\omega,\omega-1}$ 6.9 Hz, ω-CH_3), 1.26–1.80 (m, 32H, (CH_2)$_{16}$CH$_3$), 3.95 (t, 2H, $J_{\alpha,\beta}$ 6.6 Hz, α-CH_2), 6.79–7.31 (m, 14H, Ar); Anal. Calcd. for $C_{37}H_{51}ClO$: C, 81.20; H, 9.39; Cl, 6.48. Found: C, 81.43; H, 9.55; Cl, 6.69.

Methyl 6-O-trityl or methyl 6-O-(4-alkoxytrityl)-α-D-glucopyranoside (**10**)

Methyl 6-*O*-trityl-α-D-glucopyranoside was synthesized according to the method of Gómez et al.[7] Compound **9** was dried at 100°C under vacuum for 1 h. To the solution of compound **9** (48.6 mg, 0.250 mmol) in DMA (1.5 ml), compound **1** ($n = 1, 4, 12, 18$, 0.375 mmol) and pyridine (100 μl, 1.13 mmol) were added and stirred at 70°C for 2 h. The mixture was then cooled to room temperature and EtOAc was added. The solution was washed with 1 N HCl, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified on a silica gel plate developed with EtOAc/*n*-hexane (2/1, v/v) to yield compound **10** (97%) as colorless solids:

Data for $n = 4$: mp 74°–75°C; $[\alpha]_{25}^{D}$ + 47.9° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.96 (t, 3H, $J_{\omega,\omega-1}$ 7.5 Hz, ω-CH_3), 1.47 (m, 2H, -CH_2CH$_3$), 1.73 (m, 2H, -CH_2C$_2$H$_5$), 3.30–3.37 (m, 2H, H-6), 3.41 (s, 3H, -OCH$_3$), 3.45 (t, 1H, $J_{4,5}$ 9.3 Hz, H-4), 3.50 (dd, 1H, $J_{2,3}$ 9.3 Hz, H-2), 3.66 (t, 1H, $J_{5,6}$ 9.6 Hz, H-5), 3.68 (t, 1H, $J_{3,4}$ 9.3 Hz, H-3), 3.92 (t, 2H, $J_{\alpha,\beta}$ 6.6 Hz, α-CH_2), 4.74 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.80–7.46 (m, 14H, Ar); Anal. Calcd. for $C_{30}H_{36}O_7$: C, 70.84; H, 7.14. Found: C, 70.54; H, 7.27.

Data for $n = 12$: mp 67°–68°C; $[\alpha]_{25}^{D}$ + 38.8° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J_{\omega,\omega-1}$ 6.9 Hz, ω-CH_3), 1.26–1.76 (m, 20H, (CH_2)$_{10}$CH$_3$), 3.26–3.36 (m, 2H, H-6), 3.38 (s, 3H, -OCH$_3$), 3.42 (m, 1H, H-4), 3.47 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2), 3.66 (t, 1H, $J_{3,4}$ 9.3 Hz, H-3), 3.66 (m, 1H, H-5), 3.89 (t, 2H, $J_{\alpha,\beta}$ 6.6 Hz, α-CH_2), 4.72 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.78–7.46 (m, 14H, Ar); Anal. Calcd. for $C_{38}H_{52}O_7$: C, 73.52; H, 8.44. Found: C, 73.27; H, 8.73.

Data for $n = 18$: mp 64°–66°C; $[\alpha]_{25}^{D}$ + 36.1° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J_{\omega,\omega-1}$ 7.2 Hz, ω-CH_3), 1.25–1.78 (m, 32H, (CH_2)$_{16}$CH$_3$), 3.27–3.35 (m, 2H, H-6), 3.39 (s, 3H, -OCH$_3$), 3.43 (m, 1H, H-4), 3.47 (dd, 1H, $J_{2,3}$ 9.9 Hz, H-2), 3.66 (t, 1H, $J_{3,4}$ 9.3 Hz, H-3), 3.66 (m, 1H, H-5), 3.89 (t, 2H, $J_{\alpha,\beta}$ 6.6 Hz, α-CH_2), 4.72 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.78–7.46 (m, 14H, Ar); Anal. Calcd. for $C_{44}H_{64}O_7$: C, 74.96; H, 9.15. Found: C, 75.10; H, 9.19.

Results and discussion

Preparation of 4-O-alkoxytrityl chlorides (**1**)

4-Hydroxytrityl alcohol (**7**) should be a key intermediate for the present synthesis of a series of compound **1**, because compound **1** with different chain lengths could be obtained by alkylation of compound **7**. Burton et al reported the synthesis of compound **7** by the condensation reaction between benzophenone chloride and phenol,[13] but we could not obtain the compound **7** in the high yield as reported. Then we synthesized the compound **7** as follows. Compound **7** was synthesized via 4-benzyloxytrityl alcohol (**6**) prepared by the two synthetic routes **A** and **B**, as shown in Fig. 1. The route **A** follows the traditional method: methyl 4-hydroxybenzoate (**2**) was converted to 4-benzyloxybenzoate (**3**) by benzylation with benzyl bromide (BnBr) and potassium carbonate and then compound **3** was reacted with phenyl magnesium bromide (PhMgBr) to give compound **6** in ca. 70% overall yield. On the other hand, in route **B**, 4-hydroxybenzophenone (**4**) was converted to compound **6** in ca. 93% overall yield by the same reaction sequence as that of route **A**. The advantage of route **B** is that only one equivalent of flammable and moisture-

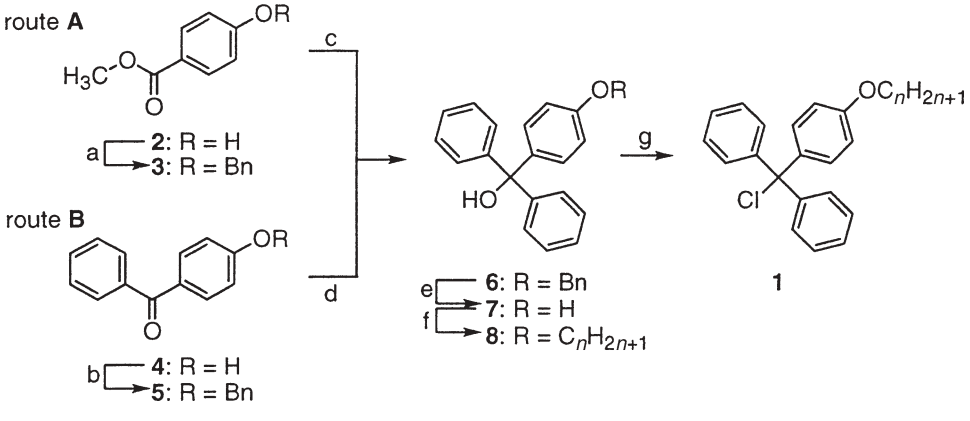

Fig. 1. Alternative routes in the synthesis of **1**. (*a*) BnBr, K_2CO_3, DMF, 60°C, overnight, 99%; (*b*) BnBr, K_2CO_3, DMF, 60°C, overnight 99%; (*c*) PhMgBr, Et_2O, benzene, reflux, 2 h, 71%; (*d*) PhMgBr, Et_2O, benzene, reflux, 2 h, 94%; (*e*) H_2, 10% Pd-C, EtOAc, room temperature, overnight, 95%; (*f*) alkyl Br, K_2CO_3, DMF, 60°C, overnight, 99%; (*g*) AcCl, benzene, reflux, 1 h, 95%

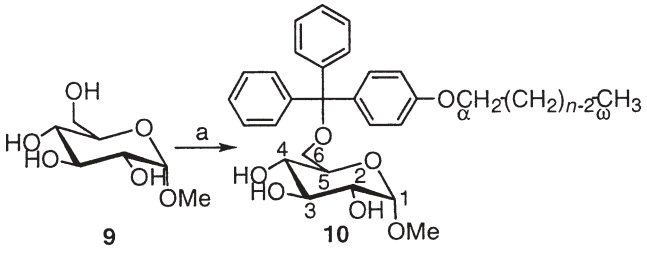

Fig. 2. Synthesis of compound series **10**. (*a*) 4-AlkoxytritylCl, pyridine, DMA, 70°C, 2 h, 97%

sensitive phenyl magnesium bromide was used and that compound **6** was obtained in high yield. Compound **6** was debenzylated with 10% Pd–C under hydrogen gas to afford compound **7** in 95% yield.

Compound **7** was treated with various *n*-alkyl bromides ($C_nH_{2n+1}Br$) with different chain lengths (n = 4, 12, 18) and potassium carbonate in *N*,*N*-dimethylformamide (DMF) to give the expected 4-alkoxytrityl alcohols (**8**). All these alkylation reactions proceeded exclusively at the phenolic hydroxyl groups in yields over 99%. Then, compound series **8** was treated with acetyl chloride (AcCl) in refluxed benzene to give a series of compound **1** in yields over 95%.[14] The structures of the trityl chloride derivatives **1** were confirmed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and elemental analyses. All derivatives were colorless solids and were found to be sufficiently stable for storage under refrigeration for at least 6 months. However, on exposure to air at room temperature, these chlorides were hydrolyzed to the corresponding alcohols.

Reactions of 4-alkoxytrityl chlorides (**1**) with methyl α-D-glucopyranoside (**9**)

A series of compound **1** was reacted with compound **9** to examine their reactivities (Fig. 2). Commercially available trityl and 4-methoxytrityl chlorides were also reacted with the glucoside to compare reactivities: the reactivity of the latter chloride has been reported to be several times higher than that of the former.[7]

All newly prepared reagents gave the expected products, methyl 6-*O*-(4-alkoxytrityl)-*α*-D-glucopyranosides (**10**), in almost quantitative yields (97%) under the same reaction conditions. This indicated that these reagents have high regioselectivity for primary hydroxyl groups of carbohydrates, almost the same reactivities as 4-*O*-methoxytrityl chlorides, and are more reactive than trityl chloride. Essentially, this means the reactivity of the series of compound **1** was not affected by the chain length. The structures of the products (**10**) were confirmed from ^{1}H NMR spectra. Thus, a series of compound **1** was found to be useful for regioselective derivatization at the primary hydroxyl group in carbohydrates. The regioselectivity of **1** was also confirmed from preliminary experiments using cellulose dissolved in a *N*,*N*-dimethylacetamide (DMA) / LiCl solvent system.[15,16]

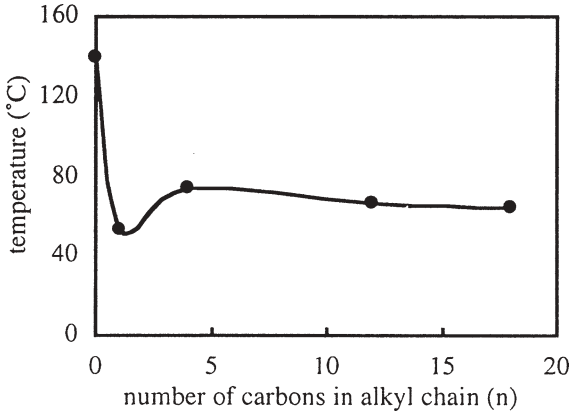

Fig. 3. Plot of the melting point of methyl 6-*O*-(4-alkoxytrityl)-*α*-D-glucopyranosides (**10**) versus the number of the carbons in the alkyl chain

Solubilities and thermal properties of compounds **10**

Generally, sugars with long alkyl chains have interesting physical properties as amphiphilic molecules, and have been studied and utilized as surfactants such as detergents or solvents of membrane proteins.[17] Their physical properties such as crystal structure,[18] liquid crystalline property,[19,20] melting point,[21] and others have also been investigated. The solubility and meltability of compounds **10** were compared. The solubilities of trityl and four 4-*O*-alkoxy (R = C_nH_{2n+1}, n = 1, 4, 12, 18) trityl derivatives of methyl *α*-D-glucopyranosides in 18 solvents, including *n*-hexane, diethyl ether, toluene, tetrahydrofuran, chloroform, acetone, ethyl acetate, acetonitrile, dichloromethane, dioxane, pyridine, DMA, DMF, ethanol, acetic acid, dimethyl sulfoxide, methanol, and water, were examined. All derivatives were insoluble in water and hexane, but were completely soluble in the other solvents examined. Thus, it is expected that the cellulose derivatives corresponding to the present 6-*O*-alkoxytrityl derivatives should be able to dissolve in these solvents to cast a film or to make fiber.[15,16]

The meltabilities of the prepared five trityl derivatives of methyl *α*-D-glucopyranoside were then examined (Fig. 3). Except for the trityl and 4-*O*-methoxytrityl derivatives, which melted at 140°C and 54°C, respectively, the newly prepared 4-*O*-alkoxyltrityl derivatives melted over a comparatively narrow temperature range from 64° to 74°C, and as the length of alkyl chain became longer, the melting point became slightly lower.

Consequently, the novel 6-*O*-alkoxyltrityl chlorides (**1**) are useful alkylating reagents with high regioselectivity for primary hydroxyl groups. These reagents may be used for the derivatization of cellulosic polysaccharides with improved solubility for further derivatizations at the secondary hydroxyl groups of the 2-*O* and 3-*O* positions.

Conclusions

A synthetic method for the synthesis of the novel reagents 4-alkoxytrityl chlorides (**1**) in high yields was developed.

These reagents were found to react with high regioselectivity toward the primary hydroxyl groups on methyl α-D-glucopyranoside (**9**), selected as a model compound, to give methyl 6-*O*-(4-alkoxytrityl)-α-D-glucopyranosides (**10**) in high yields. These products dissolved in many solvents such as diethyl ether, toluene, tetrahydrofuran, chloroform, acetone, ethyl acetate, acetonitrile, dichloromethane, dioxane, pyridine, DMA, DMF, ethanol, acetic acid, dimethyl sulfoxide, and methanol. They were insoluble in water and *n*-hexane and melted in a narrow temperature range of 64°–74°C.

The newly prepared 4-alkoxytrityl chlorides (**1**) may be conveniently used as regioselective alkyl-carrying reagents for primary hydroxyl groups in carbohydrates, especially polysaccharides such as cellulose. This is expected to impart physical properties to the products that make them more amenable to further derivatization as shown in preliminary experiments.[15,16]

Acknowledgment This investigation was supported in part by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (No. 11556301 and 14206021).

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