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Reactivity of the Reducing-End Group of Cellulose. I Preparation of Phenyl Celluloside.

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セルロースの還元性末端基の反応性 I フェニルセルロシドの調製

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Abstract

As the first step in a project to synthesize cellulose derivatives with highly regioselelective functionality, we planned to introduce a specific functional group into only the reducing-end group of a cellulose derivative. Glycosylation reactions, which are specific for the hemiacetal hydroxyl group, were carried out using cellulose triacetate (CTA) as the starting material and phenol, a simple and easily identifiable compound, as the aglycon. CTA was reacted with phenol in the presence of boron trifluoride etherate to obtain phenyl peracetyl celluloside (PPAC), which contains the phenyl group in only the reducing-end group, in high yield. Based on the molecular weight of the product, calculated both from viscosity and from the absorbance at 274 nm, it was concluded that under these reaction conditions a certain degree of depolymerization also occurs. However, it is clear that a phenyl group was introduced into each new reducing-end group formed by the cleavage of a glycosidic bond. Thus, the reaction proceeding under these conditions is a sort of phenolysis of CTA. The present method offers one means to introduce a specific functional group into only the reducing-end group of CTA.

要　旨

セルロースの高位置選択的置換誘導体の合成研究の一環として，まずセルロースの還元性末端基のみにある特定の官能基を導入することを計画した。出発物質としてセルローストリアセテート（CTA），アグリコンとして最も簡単で，同定しやすいフェノールを用いて，ヘミアセタール性水酸基に特異的であるグリコシル化反応を試みた。三フッ化ホウ素エーテル錯塩の存在下，CTAとフェノールを反応させたところ，フェノールがCTAの還元性末端基のみに導入されたフェニルパーアセチルセルロシド（PPAC）が高収率で得られた。生成物の溶液粘度および274 nmの吸光度から求めた分子量から，この反応条件下ではある程度の解重合が進行するが，グリコシド結合が切断した後に新たに生成した還元性末端基には必らずフェノールが導入されることが判明し

た。すなわち，この反応は一種の CTA のフェノール分解であり，本法は CTA の還元性末端基のみにある特定の官能基を導入するための一つの手段を提供するものと考えられる。

1. Introduction

Recent studies on the molecular design of cellulose derivatives have been directed toward the preparation of high quality or high value-added products with special functions; these products are conveniently called functional polymers. Various cellulose derivatives with special properties or abilities, such as ion exchange, chelate formation, optical resolution, catalytic activity, and so on, have been developed.[1] The preparation of these cellulose derivatives is generally accomplished by the utilization of the chemical reactivities of the primary hydroxyl group at the C_6-position and the secondary hydroxyl groups at the C_2-and C_3-positions of the repeating anhydroglucopyranosyl units in the cellulose molecule. The highly regioselective functionalization which results from the introduction of a certain functional group into only the expected position (among the C_2-, C_3-, and C_6-positions) may be extremely important in the future, but is very difficult in the present stage of development of cellulose chemistry. This problem was statistically analyzed by Spurlin.[2]

On the other hand, there is one special hydroxyl group which is a hemiacetal hydroxyl group on the reducing-end group in the cellulose molecule. The reactivity of this anomeric hydroxyl group is completely different from those of the other three alcoholic hydroxyl groups at the C_2-, C_3-, and C_6-positions.

The reaction focused on this hemiacetal character is completely regiospecific, which makes it possible to introduce the expected functional group only at the C_1-position on the cellulose molecule. Such a reaction may serve for the preparation of cellulosic two-block copolymers, which should offer a broad variety of useful properties.[3]

The reducing-end unit is a cyclic hemiacetal which in solution exists in equilibrium with the open-chain form. The open-chain form possesses an aldehyde function which is susceptible to oxidation by various reagents, such as Fehling's solution or ammonia-silver nitrate, and to nucleophilic addition by sulfur- or nitrogen-containing reagents or by carbanions. On the other hand, from the existence of the cyclic structure, the typical glycosylation reaction may be expected. This reaction has the potential to be important for the introduction of various functional groups into the reducing-end group. The glycosylation reaction of cellulose has not yet been studied in detail, although in 1980 C. Feger and H.-J. Cantow reported[3] the synthesis of cellulose-containing block copolymers with high molecular weights by a kind of glycosylation reaction. The direct proof for a glycosidic linkage between cellulose and the other polymer was not described in detail.

In the present paper, we investigated both the glycosylation of cellulose with a simple aglycon, phenol, and the characterization of the resulting phenyl celluloside. In this way we verified whether or not the general method used for the preparation of glycosides from simple sugars may also be applied to polysaccharides.

2. Experimental

2.1 Preparation of phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside

To a stirred solution of pentaacetyl-D-glucose (3.9 g, 10 mM, prepared using the acetic anhydride/sodium acetate system) and phenol (4.9 g, 50 mM) in dry methylene chloride (20 ml, see section 2.2), boron trifluoride etherate (6.3 ml, 50 mM) was added dropwise at 0℃ and the reaction mixture was stirred for 2.5 hr. The solution was diluted with ethyl acetate, washed successively with a 2N NaOH solution (until the ethyl acetate solution no longer contained phenol) and with a saturated sodium chloride solution, then dried over anhydrous Na_2SO_4, and evaporated *in vacuo* to give white crystals. The product was recrystallized from ethanol to afford colorless needles (3.4 g, 80% yield). M.p. 125-126℃ (ref.[4] 125-126℃).

2.2 Preparation of phenyl peracetyl celluloside (PPAC)

PPAC was prepared by a modification of the glycosylation method of Magnusson *et al.*[5]

Cellulose triacetate was prepared from cellulose diacetate (DS=1.8, $\overline{DP_n}$=100-120, Flakes-AC LL-10 purchased from Daicel Chemical Industries, Ltd.) by the TFAA acetylation method.[6]

A mixture of acetic acid (60 ml) and trifluoroacetic anhydride (15 ml) was heated at 50℃ for 30 min. Cellulose diacetate (9 g) which had been dried over P_2O_5 in a vacuum desiccator overnight, was added and the resulting suspension was heated at 50℃ for 12 hr. The suspension gradually became clear as the reaction proceeded. The reaction mixture was poured into 2000 ml of methanol. The resulting precipitate was washed with methanol and dried to afford a white powder (10 g). The acetyl content of this powder, determined by the method reported by Genung *et al.*[7] was 61.6% which corresponds to a DS of about 2.92. The degree of polymerization of the triacetate determined by intrinsic viscosity, was found to be 124 as described in section 2.5.

Two different amounts of boron trifluoride etherate (340 μl, 2.76 mM and 80 μl, 0.65 mM) were used for the glycosylation reactions in methylene chloride dried over activated aluminum oxide (hereafter "dry methylene chloride") and for those in methylene chloride distilled from P_2O_5 (hereafter "anhydrous methylene chloride"), respectively. Boron trifluoride etherate in 10 ml of methylene chloride was added dropwise to a stirred solution of 500 mg (0.014 mM) of cellulose triacetate ($\overline{M}_v$=25712, $\overline{DP}_v$=124, obtained above) and phenol (500 mg, 5.3 mM) in 40 ml of methylene chloride. After stirring the reaction mixture at room temperature for the prescribed period of time, the solution was poured into 2000 ml of methanol. The resulting precipitate was filtered, then suspended in 50 ml of methanol. The suspension was centrifuged (3000 r.p.m. for 5 min) and the supernatant was decanted. This centrifugation was repeated five times to remove the boron trifluoride etherate and the excess phenol used. The PPAC, obtained in almost 100% recovery, was dried over P_2O_5 in a vacuum desiccator.

2.3 Preparation of phenyl celluloside (PC)

To a stirred solution of PPAC (240 mg) dissolved in 20 ml of 20% methanol/methylene chloride (v/v), 0.1 ml of 28% sodium methoxide in methanol solution was added dropwise at room temperature. After stirring for 36 hr at room temperature under nitrogen, the reaction mixture was poured into 150 ml of methanol and the resulting precipitate was filtered. The precipitate was suspended in 50 ml of methanol, the suspension was centrifuged (3000 r.p.m. for 5 min), and the supernatant was decanted. After this centrifugation had been repeated three times the precipitate was filtered with suction to afford the expected phenyl celluloside (PC) as a colorless powder (146 mg), which was dried over P_2O_5 in a vacuum desiccator. The complete disappearance of the ester peak around 1750 cm^{-1} in the IR spectrum of this compound indicated that the acetyl groups had been completely removed.

2.4 Enzymic hydrolysis of phenyl β-D-glucoside and phenyl celluloside (PC) by Meicelase or Cellulase Type I.

Phenyl celluloside (PC) (90 mg) or phenyl glucoside (90 mg, 0.35 mM, m.p. 176℃, ref.[8] 175-176℃) which was obtained by hydrolysis of phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside with sodium methoxide, was dissolved in 18 ml of acetate buffer (0.05M, pH=4.6). To this reaction mixture, 18 mg of Meicelase (Meijiseika Inc.) or Cellulase Type I (Sigma Chemical Company) was added and incubated at 36℃. The progress of the hydrolysis was followed by high performance liquid chromatography (HPLC) under the following conditions: column: stainless steel (4.6×100 mm); packing: Cosmosil ($5C_{18}$) (Nakarai Chemicals Inc.); elution solvent: 50% methanol/water (v/v); flow rate: 0.5 ml/min; detector: UV (270 nm). The elution times of phenyl glucoside and phenol were 4.4 and 7.2 min, respectively.

2.5 Absorbance at 274 nm and intrinsic viscosity of PPAC

Two hundred mg of PPAC was dissolved in 25 ml of chloroform. The absorbance of the solution was measured at 274 nm.

Ten ml of the PPAC-chloroform solution prepared above was placed in an Ubbelohde viscometer and the relative viscosity was measured at 30℃. Both η_{sp}/c and $\ln \eta_r/c$ were plotted against the concentration. The concentration of PPAC ranged from 8.0×10^{-3} to 1.3×10^{-3} g/ml. The results were extrapolated to zero concentration in the usual manner to calculate intrinsic viscosity.

3. Results and Discussion

Many glycosylation methods have been developed and reviewed.[9] Representative methods are the Fischer method, the Koenigs-Knorr method, the Helferich method, the orthoester method and the oxazoline method.[10] Recently, the fluoride[11] and imidate[12] methods have been reported and applied for the synthesis of many naturally occuring glucosides. All of these methods, except for the Fischer method, contain two-step reactions: the activation at the anomeric position of the glycosyl donor and the glycosylation reaction with the glycosyl acceptor. In the first step, anomeric hydroxyl groups are transformed to activated functional groups, such as halides, which act as leaving groups,

but these halides or activated intermediates are usually unstable and are easily hydrolyzed to the original anomeric hydroxyl group. This is one of the reasons for the low yield in glycosylation reactions.

Methods via such unstable intermediates may not be applied for the present preparation of a celluloside because it is practically impossible to identify such an unstable intermediate which has only one functional group in a cellulose molecule. Therefore, it is more convenient for the preparation of a celluloside to use a one-step (or "direct") glycosylation rather than a two-step reaction.

Recently, Magnusson *et al.*[5] reported the simple and direct glycosylation with high yield for the acetylated glycosyl donor under acidic conditions. This method is thought to be the most promising method for the preparation of a celluloside, but the applicability for phenyl glucoside was not described. For this reason, the preparation of phenyl 2, 3, 4, 6-tetra-*O*-acetyl-*β*-D-glucopyranoside by the Magnusson method was carried out as a preliminary experiment. Peracetyl glucose was treated with phenol in the presence of boron trifluoride etherate in methylene chloride to afford the expected glucoside in 80% yield. With this result in mind the preparation of phenyl celluloside by the Magnusson method was carried out.

3. 1 Preparation and identification of phenyl peracetyl celluloside (PPAC)

The initial preparation of the PPAC was carried out as follows, based on the preliminary experiment with peracetyl glucose, but keeping in mind the generally lower reactivity of a polymer relative to that of a low molecular weight compound.

Cellulose triacetate (CTA) was treated with excess phenol (about 380 mole equivalents for PPAC) in the presence of boron trifluoride etherate (about 200 mole equivalents for PPAC) in dry methylene chloride at room temperature for 10 hours. The reaction mixture partially took the form of a swollen gel upon the addition of boron trifluoride. (Interesingly, the gel formation did not occur when anhydrous methylene chloride was used.) The product was recovered by the dilution of the reaction mixture with methanol to yield a colorless powder in almost quantitative recovery.

The infrared and ^{1}H-NMR spectra of the product were identical with those of the starting CTA. Therefore, such spectroscopic analyses are useless for the identification of phenyl celluloside.

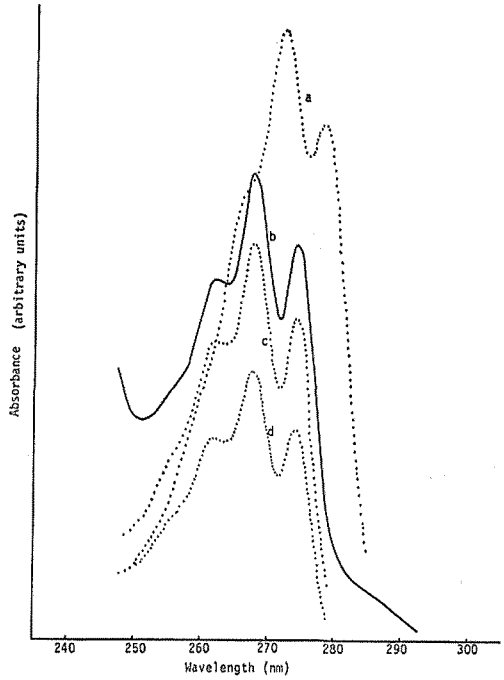

Fig. 1. UV spectra in chloroform.
a. mixture of phenol and CTA
b. phenyl peracetyl celluloside
c. phenyl peracetyl cellobioside
d. phenyl peracetyl glucoside

However, important information may be gleaned from a comparison of the respective UV spectra.

Figure 1 shows the UV spectra of a physical mixture of phenol and CTA (spectrum a), the product obtained above (spectrum b), phenyl peracetyl cellobioside (spectrum c) which was prepared by the same method used for phenyl peracetyl glucoside, and phenyl peracetyl glucoside (spectrum d) in chloroform. The UV spectrum of the mixture of phenol and CTA under neutral conditions displays two clearly defined maxima (at 278.5 nm and 272.5 nm) and one shoulder (at 267 nm). This spectrum is completely identical with that of phenol. In an alkaline dioxane solution, a maximum appeared at 293 nm. These UV-spectral properties indicate that the presence of CTA does not influence the UV spectrum of phenol. Both spectra c and d have three maxima at 274 nm ($\varepsilon=780$ and 750, respectively), 268 nm ($\varepsilon=960$ and 940) and 262 nm ($\varepsilon=720$ and 700). These peaks did not shift toward longer wavelength in an alkaline dioxane solution. The portion of spectrum b between 250 nm and 280 nm is practically the same as the corresponding portions of spectra c and d, and did not shift in an alkaline dioxane solution. These UV data indicate that phenol in the synthesized product is linked to CTA by a chemical linkage (from the comparision of spectrum b with spectrum a) and suggest that the linkage is a glycosidic bond (from the comparison of spectrum b with spectra c and d, and from consideration of the reaction mechanism). Thus, it may be concluded that the product obtained is the expected phenyl peracetyl celluloside (PPAC).

For further confirmation of the presence of the glycosidic bond, we conducted enzymic hydrolysis of the phenyl celluloside (PC) obtained by the alkaline hydrolysis of

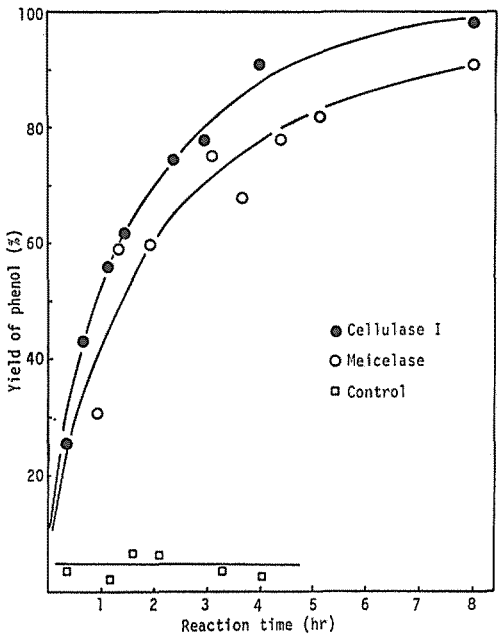

Fig. 2. Enzymic hydrolysis of phenyl glucoside at 36℃.

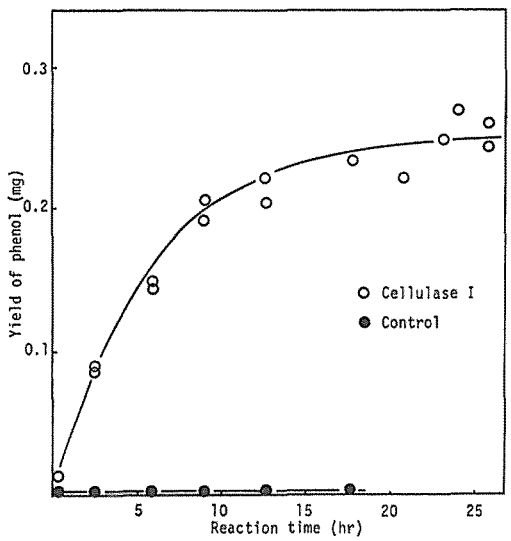

Fig. 3. Enzymic hydrolysis of PC by Cellulase I at 36℃.

PPAC. Figure 2 shows the results of a prelimimary experiment: the hydrolysis of phenyl glucoside in an acetate buffer (0.05M, pH=4.6) at 36℃ by Cellulase I or Meicelase. The production of phenol increased with the reaction time and reached a maximum of nearly 100% after 8 hours. On the other hand, no production of phenol was found in the control experiment without enzyme. Figure 3 shows the hydrolysis of PC by Cellulase I under the same conditions used for the hydrolysis of phenyl glucoside. The production of phenol increased with the progress of the reaction (as in Fig. 2), but at a lower rate. The maximum production of phenol was reached after about 25 hours. Phenol was not produced in the control experiment without enzyme. Thus, the existence of a glycosidic bond between cellulose and phenol was verified experimentally. Unfortunately it is not possible to calculate the yield of the glycosylation reaction based upon the amount of phenol produced by the present enzymic hydrolysis because the hydrolysis reaction does not proceed quantitatively. Furthermore, it was reported that a small quantity of the corresponding α-anomer is produced by the Magnusson method, and that the yield of the α-anomer increases with higher reaction temperature.[5] It was found from a preliminary experiment using phenyl α-D-glucoside that the α-glucosidic bond was not cleaved by the Cellulase I used in the present hydrolysis.

3.2 Effect of the reaction conditions on the DP of PPAC

Boron trifluoride etherate, which is a relatively strong Lewis acid, may act as an acidic catalyst for the depolymerization of cellulose. With this consideration in mind several PPACs were prepared under different reaction conditions and the effects of the reaction conditions on the depolymerization were investigated. The results are summarized in Table 1.

Table 1. Effect of reaction conditions on the $\overline{DP}$ of PPAC.

Reaction No.	R.T.	$[\eta]$	$\overline{DP}_v$	A(274)	$\overline{DP}$(274)
1	1	53.5	115	0.20	104
2	3	50.3	104	0.20	104
3	5	44.5	94	0.22	95
4	10	37.6	76	0.28	74
5	30	32.0	66	0.47	51
6	1	50.5	104	0.17	123
7	3	41.5	87	0.22	95
8	5	36.3	87	0.26	80
9	10	27.5	56	0.37	56
10	10	15.0	28	0.59	35

R.T. : reaction time, $[\eta]$: intrinsic viscosity
$\overline{DP}_v$: calculated from $[\eta]$
A(274) : optical density at 274 nm
$\overline{DP}$(274) : DP calculated from A(274)
#1-#5 : CTA(500 mg)/phenol(500 mg)/BF_3-Et_2O (340 μl) in dry CH_2Cl_2
#6-#9 : CTA(500 mg)/phenol(500 mg)/BF_3-Et_2O (80) μl) in anhydrous CH_2Cl_2
#10 : CTA(500 mg)/phenol(500 mg)/BF_3-Et_2O (340 μl) in anhydrous CH_2Cl_2
BF_3-Et_2O : boron trifluoride etherate

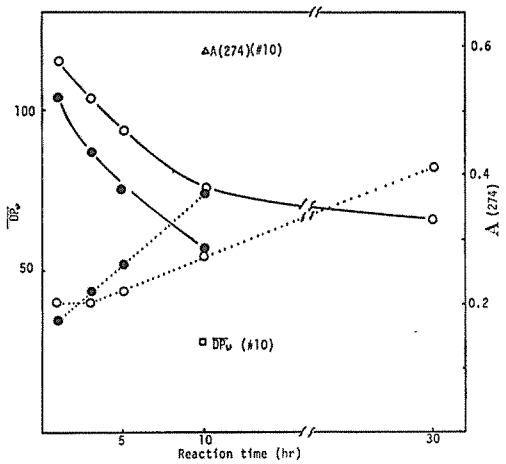

Fig. 4. Effect of reaction conditions on the $\overline{DP}_v$ and A(274) of PPAC.
1(○——○) : $\overline{DP}_v$ (#1-#5)
2(●——●) : $\overline{DP}_v$ (#6-#9)
3(○·····○) : A(274) (#1-#5)
4(●·····●) : A(274) (#6-#9)

The reaction was carried out both in dry methylene chloride (#1-#5) and in anhydrous methylene chloride (#6-#10) to determine the effect of water on the activity of boron trifluoride etherate. Two different amounts of boron trifluoride etherate (340μl in #1-#5 and #10, 80μl in #6-#9) were used. The degree of polymerization of each sample was calculated from the intrinsic viscosity [η] and from the absorbance at 274 nm (A(274)). In the first case the molelular weight (M) was calculated from the equation :[13]

$$[\eta]_{\text{chloroform}} = 4.5 \times 10^{-3} M^{0.9} \quad (1)$$

In the second case, for the determination of the $\overline{DP}$ from the A(274)-value, it is necessary to assume that all of the reducing-end groups of PPAC are substituted with phenol (i.e., the glycosylation reaction proceeds in 100% yield), and that the ε-value of PPAC at 274 nm is the same as that of phenyl peracetyl-β-D-glucoside (ε=750). The $\overline{DP}$ (274) may then be calculated by the following equation:

$$\overline{DP}(274) = 750 \times c/A(274)/288 \quad (2)$$

here, c =concentration of PPAC (g/l), A(274)=absorbance at 274 nm, 288=moleculer weight of the 2,3,6-tri-O-acetyl-β-glucopyranosyl residue. A comparison of the $\overline{DP}_v$ with the $\overline{DP}$ (274) obtained for each sample (Table 1) indicates very good agreement. These data suggest that the above two assumptions used for the calculation of DP(274) are valid.

As shown in Fig. 4, the $\overline{DP}_v$ decreases almost exponentially (curves 1 and 2), but the A(274) increases linearly (curves 3 and 4) with the reaction time. The degree of these changes depend on the amount of boron trifluoride etherate used; extreme depolymerization occured in experiment #10. Since the quantity $1/\overline{DP}$, which corresponds to the number of chain breaks and is proportionl to A(274) (equation 2), was found to increase linearly with time, the rate of the reaction did not change with time. Thus, the kinetics of the present reaction are zero order. This is a characteristic of the homogeneous hydrolysis of cellulose[14]. On the other hand, the slope of the straight line obtained from A(274)-time plots (or $1/\overline{DP}$-time plots) indicates the rate of the reaction. The rate of the reaction using a ratio of about 50 mole equivalents of Lewis acid in anhydrous methylene chloride was found to be about twice that of the reaction using about 200 mole equivalents of Lewis acid in dry methylene chloride. Qualitatvely, it is clear that the presence of a trace amount of water in the reaction solvent (i.e. dry methylene chloride vs. anhydrous methylene chloride) lowered the rate of the depolymerization reaction in spite of a four-fold increase in the concentration of the boron trifluoride etherate (i.e. 200 mole equivalents vs. 50 mole equivalents). Further experiments are necessary in order to quantify the separate effects due to water and to the Lewis acid.

4. Conclusions

When the Magnusson glycosylation method is applied for the modification of CTA, both the expected glycosylation and depolymerization proceed with time. However, phenol may be introduced into each reducing-end group newly formed after acid-catalyzed cleavage

of a glycosidic bond in CTA ; the efficiency of the introduction of phenol approaches 100% under certain conditions. Therefore, the overall reaction may be described as phenolysis.

Thus, it is possible that the highly regioselective introduction of a special functional group into the reducing-end group of CTA may be achieved under Magnusson's glycosylation conditions by reacting CTA with phenol derivatives containing the special functional group. In that case, the phenol functions as a kind of carrier to transport the special functional group into the CTA molecule. A further investigation into this possibility is now in progress.

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