# Reaction of 6-Bromo-6-deoxycellulose with Thiols in Lithium Bromide–*N,N*-Dimethylacetamide

NOBUYOSHI AOKI,[1,*] KEN-ICHI FURUHATA,[1,†] YASUO SAEGUSA,[2] SHIGEO NAKAMURA,[2] and MUNENORI SAKAMOTO[1]

[1]Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152, Japan, and [2]Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama, 221, Japan

SYNOPSIS

Nucleophilic substitution reactions of 6-bromo-6-deoxycelluloses of high degrees of substitution with eight thiols having functional groups such as carboxyl and amino groups were studied under homogeneous conditions in LiBr–*N,N*-dimethylacetamide in the presence of triethylamine. The reactions under the homogeneous conditions proceeded more extensively than those run under heterogeneous conditions in aqueous alkaline solutions. The reactivity of thiols was found to increase with increasing acidity of the mercapto groups of the thiols. Reaction products with 2-mercaptobutanedioic acid and with 2-mercaptobenzoic acid were soluble in alkaline and neutral water but not in 1 *N* HCl, while the reaction products with 2-aminoethanethiol did not dissolve even in 1 *N* HCl. The reaction products with cysteine showed amphoteric behavior. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

We have reported reactions of chloro- and bromodeoxycelluloses with various thiols under heterogeneous conditions in aqueous alkaline solutions, where bromodeoxycellulose was more reactive than chlorodeoxycellulose.[1] Methanethiol, benzenethiol, 2-mercaptoethanol, and 2-aminoethanethiol reacted with halodeoxycelluloses in 40–64% conversions, while reactions of carboxyl-containing thiols including cysteine with halodeoxycelluloses did not proceed much. Halodeoxycelluloses are soluble in lithium chloride– or lithium bromide–*N,N*-dimethylacetamide (DMA) without any pretreatment,[2,3] required for dissolution of cellulose itself in these solvent systems.

In this article we report the reactions of 6-bromo-6-deoxycellulose (Cell-Br) with various thiols under homogeneous conditions, mostly in the presence of triethylamine (TEA), in lithium bromide–DMA. Under appropriate and mild conditions, the nucleophilic substitutions took place in conversions higher than those of the corresponding reactions under heterogeneous conditions in aqueous alkaline solutions.[1] GC–MS analysis was carried out after converting hydrolyzates of the reaction products to methyl esters of trifluoroacetyl derivatives. The structures of products were also studied by NMR spectroscopy.

## EXPERIMENTAL

### Materials

Microcrystalline cellulose (Art 2331 cellulose mikrokristallin™, Merck) was used after drying under reduced pressure. DMA was dried with calcium hydride and distilled under reduced pressure. Anhydrous LiBr was dried at 180°C under reduced pressure before use. TEA was distilled and stored over potassium hydroxide. Commercial thiols were used without further purification.

* Present address; Kanagawa Industrial Technology Research Institute, 705-1, Shimoimaizumi, Ebina, 243-04, Japan.
† To whom correspondence should be addressed.

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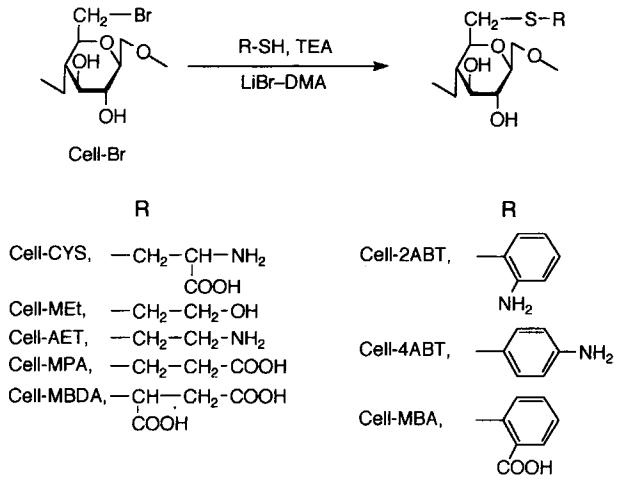



**Scheme 1**

## Bromination of Cellulose

Microcrystalline cellulose was brominated as previously reported[2] with *N*-bromosuccinimide and triphenylphosphine in LiBr–DMA.

## Dissolution of Cell-Br in LiBr–DMA and Reaction with Thiols

Typical procedure for dissolution of Cell-Br and reaction with a thiol is as follows: Cell-Br (0.1 g) was added to 10 mL of 2.3*M* LiBr–DMA at 70°C. The mixture was stirred for 1 h to give a clear solution. The solution was cooled to the reaction temperature and a thiol and TEA were added to the solution. The reaction solution was stirred for a prescribed time and then poured into an excess amount of acetone. The obtained precipitates were collected by centrifugation and dialyzed against distilled water for 3 days. In the case of the reaction with cysteine, the obtained sample was dialyzed against aqueous $Na_2CO_3$ solution (pH 11.5) for 3 days to remove remaining sparingly soluble cysteine before dialyzing against water. In some cases, the content in the dialysis tube was separated by centrifugation into the precipitates and the solution, and from both reaction products were collected by freeze drying.

## Analyses

### *Elemental Analysis*

Bromine and sulfur contents were determined by an oxygen-flask combustion method.[4]

### *IR Spectra*

Infrared spectra were recorded in KBr disks on a Fourier-transform IR spectrophotometer FT/IR-3

**Table I Effect of Base on the Reaction of Cell-Br with CYS[a]**

| Exp No. | Base | | Temp °C | Cell-Br | | SH/Br | Remark[b] | Yield % | S% | Br% | $DS_s$ | $DS_{Br}$ | ΔDS | Conv% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Code | mL | | $DS_0$ | g | | | | | | | | | |
| 1 | — | — | 30 | 0.70 | 0.10 | 2.4 | p | 41.7 | 0.50 | 19.24 | 0.03 | 0.45 | 0.21 | 4 |
| 2 | TEA | 1.0 | 30 | 0.86 | 0.10 | 2.0 | p | 5.8 | 4.30 | 10.28 | 0.27 | 0.26 | 0.34 | 31 |
| | | | | | | | d | 51.2 | 7.04 | 7.50 | 0.49 | 0.21 | 0.16 | 57 |
| | | | | | | | p + d | 57.0 | | | 0.47 | 0.21 | 0.18 | 54 |
| 3 | | 2.0 | | 0.86 | 0.10 | 2.0 | p + d | 71.0 | 7.60 | 9.55 | 0.56 | 0.28 | 0.01 | 66 |
| 4 | | 3.0 | | 0.86 | 0.10 | 2.0 | p + d | 99.7 | 6.30 | 7.08 | 0.42 | 0.19 | 0.25 | 49 |
| 5 | TEA | 1.0 | 50 | 0.86 | 0.20 | 2.0 | p | 13.0 | 3.89 | 9.98 | 0.24 | 0.24 | 0.34 | 28 |
| | | | | | | | d | 75.4 | 5.35 | 13.29 | 0.36 | 0.37 | 0.13 | 42 |
| | | | | | | | p + d | 88.4 | | | 0.35 | 0.35 | 0.16 | 41 |
| 6 | | 2.0 | | 0.83 | 0.17 | 2.0 | p | 47.2 | 7.00 | 6.83 | 0.48 | 0.19 | 0.16 | 58 |
| | | | | | | | d | 22.5 | 6.86 | 8.08 | 0.48 | 0.23 | 0.13 | 58 |
| | | | | | | | p + d | 69.7 | | | 0.48 | 0.20 | 0.15 | 58 |
| 7 | | 3.0 | | 0.83 | 0.10 | 2.0 | p | 32.7 | 7.58 | 4.57 | 0.52 | 0.13 | 0.18 | 63 |
| | | | | | | | d | 52.9 | 7.17 | 5.99 | 0.49 | 0.16 | 0.17 | 59 |
| | | | | | | | p + d | 85.6 | | | 0.50 | 0.15 | 0.18 | 61 |
| 8 | NaOH | 0.2 (g) | 40 | 0.52 | 0.20 | 2.0 | p | 88.6 | 1.29 | 13.18 | 0.08 | 0.31 | 0.14 | 15 |
| | | | | | | | d | 6.6 | 6.22 | 11.80 | 0.46 | 0.35 | −0.29 | 88 |
| | | | | | | | p + d | 95.2 | | | 0.10 | 0.31 | 0.11 | 19 |

[a] Reactions were carried out in 10 mL of LiBr-DMA for 24 h.

[b] Reaction products were obtained as precipitates (p) and/or dissolved fractions (d) after dialysis. The data for the combined products (p + d) were calculated from those of p and d fractions. In some cases, the two fractions (p + d) were not separated as in Experiments 3 and 4.

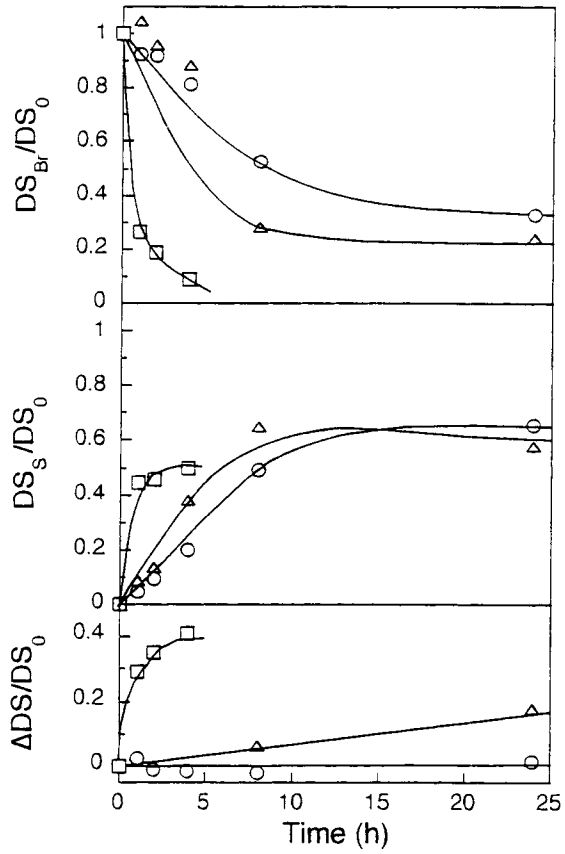



**Figure 1** Reactions of Cell-Br (1 mg/mL of DMA) with CYS ([SH]/[Br in Cell-Br], 2 mol/mol) at 30 (○), 50 (△), and 70°C (□).

(JASCO Ltd.). A spectrum of ambient air was used for the reference.

### $^{13}C$ NMR

$^{13}C$ NMR spectra were recorded on a JNM-A500 spectrometer (125.65 MHz for $^{13}C$, JEOL Ltd.). $D_2O$ was used as a solvent and a small amount of NaOD in $D_2O$ was added to the solution to dissolve the cellulose samples completely. Measurements were carried out at 60°C with sodium 2,2'-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard. *S*-Ethylcysteine[5] and ethylthiobutanedioic acid[6] were used as model compounds for corresponding cellulose derivatives.

### *GC and GC–MS Analyses*

Reaction products (5 mg) were hydrolyzed with $H_2SO_4$ and the hydrolyzates were converted to trifluoroacetyl derivatives[1,7] for GC and GC–MS analyses. The conditions for hydrolysis and trifluoroacetylation were the same as those reported previously.[1,2]

Hydrolyzates of samples containing carboxyl groups were treated with HBr–MeOH before trifluoroacetylation. Neutralized and dried hydrolyzates were mixed with dichloromethane (50 mL) and HBr–MeOH (11.7 wt %, 50 mL) in a Reacti Vial and the mixture was refluxed for 10 min. The solvent was removed under nitrogen stream at 60°C. Then the trifluoroacetylation was repeated twice in a usual way.

GC chromatograms were recorded on a Shimadzu GC-4BM gas chromatograph. A Shimadzu LKB-9000 gas chromatograph–mass spectrometer was used for the GC–MS analysis. The stationary phase for GC and GC–MS was SE-30 coated on Gas Chrom Q (100–120 mesh, 3 w t%). The column temperature was raised from 60°C at 3°C/min. Other operation conditions of the instruments were the same as those previously reported.[2]

## RESULTS AND DISCUSSION

Cell-Br samples used in this study were synthesized under homogeneous conditions by the method previously reported.[2] Only C-6 hydroxyl groups were substituted, and the degree of substitution by bromine of Cell-Br ($DS_0$) used for the treatment with thiols ranged from 0.52 to 0.87. The reactions of Cell-Br were studied in LiBr–DMA with L-cysteine (CYS), 2-mercaptoethanol (MEt), 2-aminoethanethiol (AET), 3-mercaptopropanoic acid (MPA), racemic 2-mercaptobutanedioic acid (MBDA), 4-aminobenzenethiol (4ABT), 2-aminobenzenethiol (2ABT), and 2-mercaptobenzoic acid (MBA), as shown in Scheme 1.

### Reaction Conditions

The effects of reaction conditions were studied in detail for the reaction with CYS, which contains both amino and carboxyl groups. The reactions between polymers containing bromine and CYS gave amphoteric chelating materials[9] in one step. Substitution of bromine atom in Cell-Br with CYS was attempted in LiBr–DMA with or without a base at 30 and 50°C. The results are shown in Table I. CYS is insoluble in DMA but soluble in LiBr–DMA. Consequently, the reaction system was homogeneous. Degrees of substitution by bromine ($DS_{Br}$) and by the thiol moiety ($DS_S$) were calculated from the bromine and sulfur contents of the reaction products and $DS_0$, as described in the previous article.[1] The $DS_S/DS_0$ values can be regarded as conversions of bromine to sulfur. The difference ($\Delta DS$)

**Table II Reactions[a] of Cell-Br with Aliphatic Thiols**

| No. | Thiol Code | Thiol mmol | Cell-Br g | Cell-Br $DS_0$ | SH/Br mol/mol | TEA mL | DMA mL | Temp °C | Remark[b] | Yield % | DSS | $DS_{Br}$ | ΔDS | Conv % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | MEt | 4.97 | 0.1 | 0.83 | 2.0 | 2 | 10 | 30 | p | 80.5 | 0.37 | 0.51 | −0.06 | 44.6 |
| 10 | | 14.2 | 0.1 | 0.86 | 35.6 | 2 | 10 | 30 | p | 76.3 | 0.71 | 0.13 | 0.02 | 82.6 |
| 11 | AET | 0.78 | 0.1 | 0.83 | 2.0 | 0 | 10 | 30 | d | — | 0.72 | 0.30 | −0.19 | 86.7 |
| 12 | | 0.83 | 0.1 | 0.87 | 2.1 | 2 | 10 | 30 | p + d | 102.2 | 0.55 | 0.10 | 0.22 | 63.2 |
| 13 | | 1.67 | 0.2 | 0.70 | 2.5 | 4 | 20 | 50 | p | — | 0.48 | 0.07 | 0.15 | 68.6 |
| 14 | | 3.11 | 0.1 | 0.83 | 8.0 | 2 | 10 | 30 | d | 73.5 | 0.57 | 0.36 | −0.07 | 68.7 |
| 15 | | 229 | 1.5 | 0.81 | 24.7 | 60 | 150 | 50 | p | 53.1 | 0.63 | 0.02 | 0.17 | 77.8 |
| 16 | MPA | 3.67 | 0.1 | 0.83 | 2.0 | 2 | 10 | 30 | p | 70.5 | 0.06 | 0.89 | −0.13 | 7.2 |
| 17 | | 11.5 | 0.1 | 0.87 | 28.7 | 4 | 10 | 30 | p + d | 127.0 | 0.49 | 0.11 | 0.27 | 56.3 |
| 18 | | 23.0 | 0.2 | 0.70 | 34.0 | 4 | 20 | 50 | p | 39.9 | 0.30 | 0.05 | 0.35 | 42.9 |
| | | | | | | | | | d | 64.7 | 0.92 | 0.11 | −0.34 | 131.4 |
| | | | | | | | | | p + d | 104.6 | 0.69 | 0.09 | −0.08 | 98.6 |
| 19 | | 115 | 1.0 | 0.81 | 32.9 | 40 | 100 | 50 | p | 43.0 | 0.71 | 0.07 | 0.03 | 87.7 |
| | | | | | | | | | d | 1.7 | 0.53 | 0.09 | 0.19 | 65.4 |
| | | | | | | | | | p + d | 44.7 | 0.70 | 0.07 | 0.04 | 86.4 |
| 20 | MBDA | 0.78 | 0.1 | 0.83 | 2.0 | 2 | 10 | 30 | p | 78.1 | 0.08 | 0.82 | −0.07 | 9.6 |
| 21 | | 0.78 | 0.1 | 0.83 | 2.0 | 4 | 10 | 30 | d | 100.0 | 0.51 | 0.25 | 0.07 | 61.4 |
| 22 | | 1.97 | 0.2 | 0.83 | 2.5 | 8 | 30 | 50 | d | 93.5 | 0.47 | 0.24 | 0.11 | 56.6 |

[a] Reactions were carried out for 24 h.
[b] See Table I.

between $DS_0$ and the sum of $DS_S$ and $DS_{Br}$ can be regarded as the extent of the formation of 3,6-anhydroglucose and/or 5,6-glucosene units as a results of a side reaction, intramolecular dehydrobromination of Cell-Br in the presence of a base.[3]

When the reaction was run without a base at 30°C (Experiment 1), the reaction product was recovered as precipitates at the end of dialysis for purification of the product. The sulfur and bromine analyses showed that the substitution took place to a very limited extent. When the reaction was run in the presence of TEA (Experiment 2), a very small amount of precipitates were collected after dialysis. The remaining solution in the dialysis tube was dried by freeze drying and the dissolved product was recovered. The products precipitated (p) and dissolved (d) in the tube were analyzed separately. The conversions for d and p were much higher than that for the sample obtained in the absence of TEA. The weight-average conversion and other data for the total product (p + d) recovered were calculated and shown in the table. The effects of the amount of TEA used and the reaction temperature were studied. In some cases (Experiments 3 and 4), the pre-

**Table III Reactions[a] of Cell-Br with Aromatic Thiols**

| No. | Thiol Code | Thiol mmol | Cell-Br g | Cell-Br DS | SH/Br mol/mol | TEA mL | DMA mL | Temp °C | Remark[b] | Yield % | DSS | $DS_{Br}$ | ΔDS | Conv % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | MBA | 0.78 | 0.1 | 0.83 | 2.0 | 2 | 10 | 30 | d | 102.7 | 0.64 | 0.18 | 0.01 | 77.1 |
| 26 | | 0.78 | 0.1 | 0.83 | 2.0 | 4 | 10 | 30 | d | — | 0.59 | 0.14 | 0.09 | 71.1 |
| 27 | 2ABT | 0.77 | 0.1 | 0.81 | 2.0 | 2 | 10 | 30 | p | 68.0 | 0.76 | 0.07 | −0.02 | 93.6 |
| 28 | 4ABT | 0.76 | 0.1 | 0.81 | 2.0 | 2 | 10 | 30 | p | 84.9 | 0.76 | 0.09 | −0.04 | 93.5 |
| 29 | | 0.78 | 0.1 | 0.83 | 2.0 | 2 | 10 | 30 | p | 87.1 | 0.84 | 0.11 | −0.12 | 101.2 |
| 30 | | 1.05 | 0.1 | 0.52 | 3.9 | 2 | 10 | 30 | p | 74.5 | 0.42 | 0.04 | 0.06 | 80.8 |
| 31 | | 2.66 | 0.1 | 0.52 | 9.9 | 2 | 10 | 30 | p | 87.7 | 0.45 | 0.03 | 0.03 | 86.5 |
| 32 | | 19.1 | 1.0 | 0.81 | 5.0 | 20 | 100 | 50 | p | 72.0 | 0.79 | 0.02 | 0.00 | 97.5 |

[a] Reactions were carried out for 24 h.
[b] See Table I.

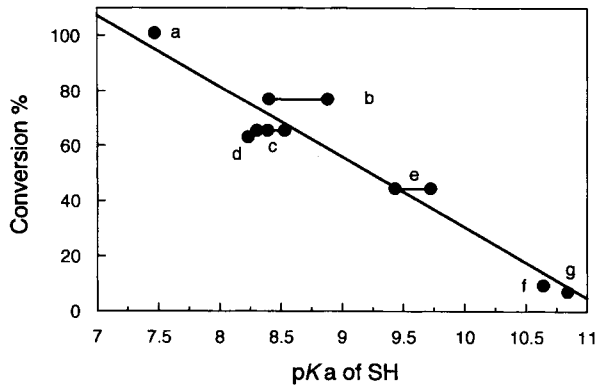



**Figure 2** Relation between pKa of mercapto group in thiol and conversion of bromine of Cell-Br (1 mg/mL of DMA) when treated with thiol ([SH]/[Br in Cell-Br], 2 mol/mol) in the presence of TEA (0.2 mL/mL of DMA) at 30°C for 24 h: (a) 4ABT; (b) MBA; (c) AET; (d) CYS; (e) MEt; (f) MPA; (g) MBDA. The pKa values plotted here were measured at 25°C in water[11-14] except for 4ABT, which was measured at 20°C in ethanol–water (20 v/v%).[15]

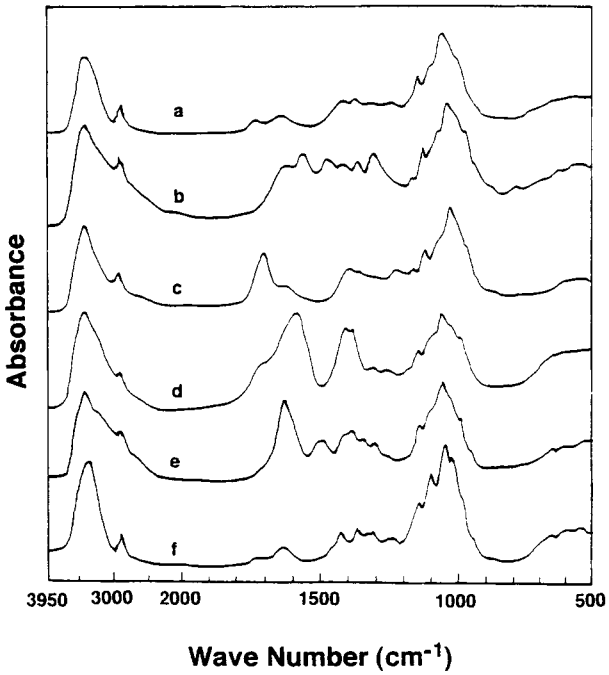



**Figure 3** IR spectra of Cell-Br treated with aliphatic thiols: (a) Cell-MEt ($DS_S$ = 0.71, $DS_{Br}$ = 0.13); (b) Cell-AET ($DS_S$ = 0.63, $DS_{Br}$ = 0.02); (c) Cell-MPA ($DS_S$ = 0.71, $DS_{Br}$ = 0.07); (d) Cell-MBDA ($DS_S$ = 0.47, $DS_{Br}$ = 0.24); (e) Cell-CYS ($DS_S$ = 0.56, $DS_{Br}$ = 0.28); (f) Cell-Br ($DS_{Br}$ = 0.83).

cipitated and dissolved products were collected together. When 1 mL of TEA was used, the conversion of the precipitated product was only ca. 30%. When 2 or 3 mL of TEA was used, the conversions of both precipitated and dissolved products became 50% or higher. The role of TEA on the substitution reaction is considered (1) to help conversion of thiol groups into more reactive thiolate anions, and (2) to scavenge HBr formed.

Although sodium hydroxide was almost insoluble in a solvent system, $SO_2$–diethylamine–dimethylsulfoxide, it catalyzed the etherification of cellulose in the solvent system.[10] The effect of sodium hydroxide, which was also hardly soluble in LiBr–DMA, on the reaction of Cell-Br with CYS was studied (Experiment 8). In the present case, the catalytic effect of sodium hydroxide was low.

The time courses of the reactions at 30, 50, and 70°C are shown in Figure 1. $DS_{Br}$ and $DS_S$ values plotted here are weight-average values of p and d parts of each product. At all temperatures studied, $DS_{Br}$ decreased and $DS_S$ increased as the reaction proceeded. At higher temperatures, the substitution took place more rapidly than at lower temperatures. The plots of $\Delta DS$ show, however, that the rate of the intramolecular dehydrobromination also increased with increasing temperature. The extent of

**Table IV Solubilities[a] of Some Cellulose Derivatives**

| | | | HCl | | | NaOH | |
|---|---|---|---|---|---|---|---|
| Sample | DSS | Remark[b] | 1 *N* | pH 5.0 | $H_2O$ | pH 9.0 | 1 *N* |
| Cell-AET | 0.72 | d | − | − | − | − | − |
| Cell-MPA | 0.92 | d | − | − | − | − | ± |
| Cell-MBDA | 0.47 | d | − | + | + | + | + |
| Cell-CYS | 0.55 | d | ± | − | − | − | ± |
| Cell-4ABT | 0.84 | d | − | − | − | − | − |
| Cell-MBA | 0.64 | d | − | + | + | + | + |

[a] 10 mg sample/10 mL.
+, soluble; ±, swollen or partially soluble; −, insoluble.
[b] See Table I.

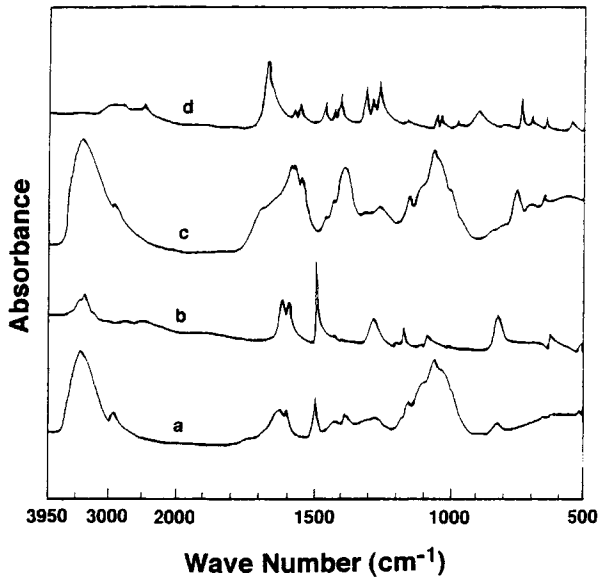



**Figure 4** IR spectra of aromatic thiols and Cell-Br treated with them: (a) Cell-4ABT ($DS_{Br}$ = 0.04, $DS_S$ = 0.42); (b) 4ABT; (c) Cell-MBA ($DS_{Br}$ = 0.14, $DS_S$ = 0.59); (d) MBA.

dehydrobromination was the lowest at 30°C among the temperatures studied.

## Reaction with Other Thiols

Reactions of Cell-Br with various thiols were studied in the presence of TEA (Tables II and III). The effect of TEA was dependent on the functional groups of the thiol molecules: TEA had no positive effect for the reaction with amino-bearing AET, while a larger amount of TEA was necessary for the carboxyl-bearing thiols.

To compare the reactivities of thiols, the conversions obtained under the same conditions ([SH]/[Br in Cell-Br] = 2, at 30°C for 24 h, in Tables I, II, and III) are plotted in Figure 2 against pKa values of the mercapto groups.[11-14] The pKa values used here are those measured under the same conditions unless otherwise noted. When two or three pKa values were reported for a thiol, the data are shown as plots linked by a horizontal line in Figure 2. A good correlation is observed between the pKa values of thiols, in other words, acidities of mercapto groups, and the conversion. In the case of the reaction under heterogeneous conditions in the aqueous alkaline solution, on the other hand, such a simple correlation was not observed.[1]

This correlation makes it possible to estimate the reactivities of various thiols in LiBr–DMA; for example, 4-mercaptobenzoic acid will be a more suitable reagent for the introduction of carboxyphenyl groups into cellulose than MBA because the acidity of the mercapto group of *o*-isomer (MBA) is reduced by the neighboring carboxyl group.[15] The observation that thiols with less acidic mercapto groups required a larger amount of TEA suggests that the most important role of TEA was to dissociate mercapto group rather than to scavenge acid.

In addition to the amount of TEA, the amounts of thiols and the reaction temperature affected the reaction. By the control of these reaction parameters, it was possible to obtain highly modified thiodeoxycellulose derivatives from a variety of thiols under relatively mild conditions, and this reaction will be useful for the introduction of functional groups into cellulose.

The solubilities of the reaction products of Cell-Br with various thiols during dialysis seemed to depend on the nature of *S*-substituents, the extent of the substitution, and the molecular weights of the products. The reaction products of high $DS_S$ values with MEt, 2ABT, and 4ABT were obtained as precipitates in high yields. Introduction of hydroxyl or aromatic amino groups showed little effect on the solubility in neutral water. The reaction product of a high $DS_S$ with MBA was obtained from the aqueous solution in a high yield. The reaction products of $DS_S$ around 0.5 with MBDA were obtained in the dissolved state but the reaction products of $DS_S$ below 0.1 were obtained as precipitates.

The solubilities of some of the reaction products obtained as dissolved state were studied after being freeze dried (Table IV). Except for Cell-MBDA and Cell-MBA, the products could not be redissolved in neutral water. All the samples containing carboxyl groups dissolved in 1 *N* NaOH, while amino-containing derivatives, Cell-AET and Cell-4ABT, did not dissolve in 1 *N* HCl. Cell-CYS showed the amphoteric behavior: it was almost soluble both in acidic and alkaline solutions. The dissolved Cell-CYS could be precipitated by neutralization and the dissolution-precipitation cycle could be repeated.

## IR Spectra

IR spectra of the samples treated with aliphatic thiols are shown in Figure 3. Peaks were assigned based on the data summarized in the literature.[16] The spectrum of Cell-MEt in Figure 3(a) had no peaks distinguishable from that of Cell-Br [Fig. 3(f)] even for the relatively high $DS_S$ because the thiol moiety had only functional groups common with Cell-Br. Spectra of other samples showed that the expected functional groups were introduced into

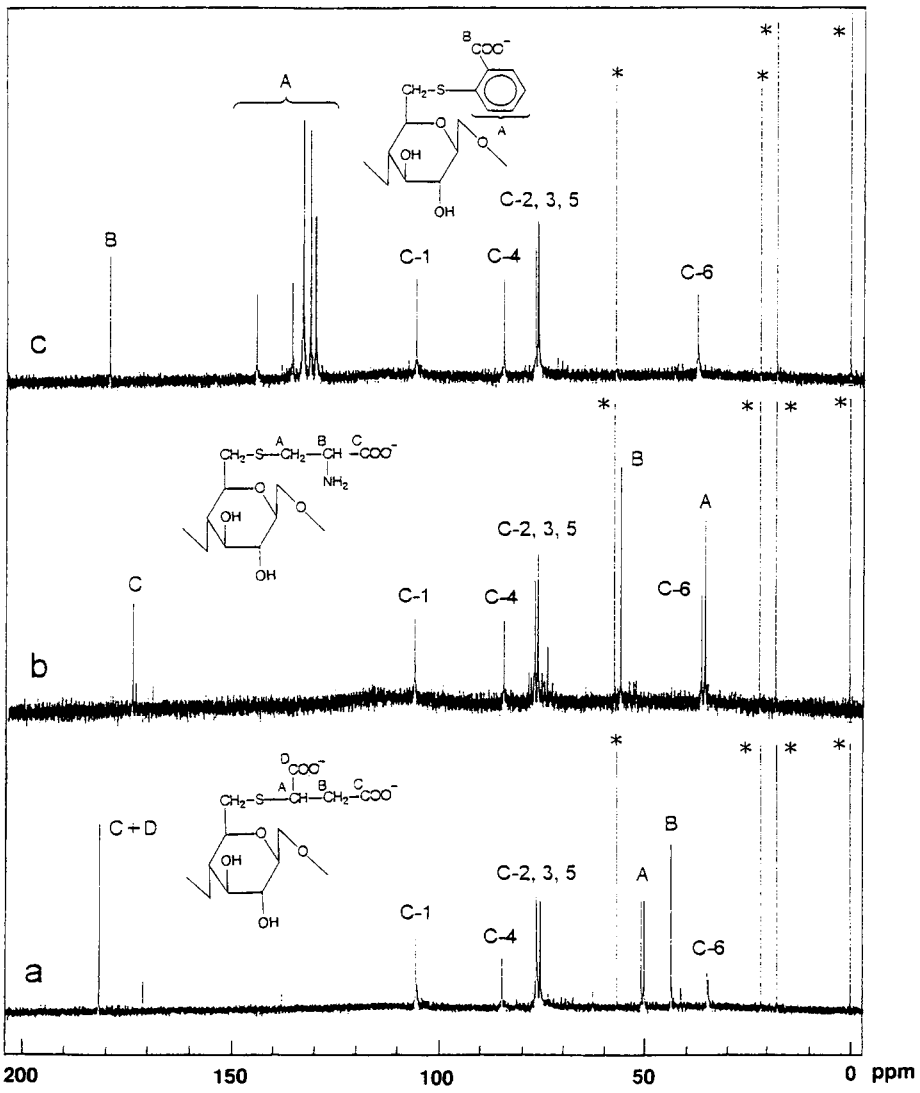



**Figure 5** $^{13}C$ NMR spectra of: (a) Cell–MBDA ($DS_S$ = 0.51, $DS_{Br}$ = 0.14); (b) Cell–CYS ($DS_S$ = 0.69, $DS_{Br}$ = 0.13); and (c) Cell–MBA ($DS_S$ = 0.64, $DS_{Br}$ = 0.18). *Peaks due to DSS.

cellulose chains by the thiol treatments. The spectrum of Cell-AET [Fig. 3(b)] showed absorptions at 3000, 1626, 1566, and 1394 $cm^{-1}$. These peaks indicated that the Cell-AET contained amino groups in the $NH_3^+$ form to some extent. A peak at 1729 $cm^{-1}$ [Cell-MPA, Fig. 3(c)] was assigned to $\nu_{C=O}$ in free carboxylic acid. New peaks at 1585 and 1709 $cm^{-1}$ on the spectrum of Cell-MBDA [Fig. 3(d)] were ascribed to C=O ($\nu_{as}$) in carboxylate anion and $\nu_{C=O}$ in dimerized carboxylic acid, respectively. A part of carboxyl groups retained the carboxylate form because this sample was dialyzed against a $Na_2CO_3$ solution just before dialysis against water. A broad absorption centered approximately at 3000 $cm^{-1}$ ($\nu_{N-H}$), a relatively strong absorption at 1634 $cm^{-1}$ (overlapping $\nu_{C=O}$ of carboxylate, and $\delta_{N-H}$ of $NH_3^+$), and an absorption at 1501 $cm^{-1}$ ($\delta_{N-H}$ of $NH_3^+$) were observed on the spectrum of Cell-CYS [Fig. 3(e)]. This assignment agrees with the structure of a usual amino acid in dipolar form.

IR spectra of the samples obtained with aromatic thiols are shown in Figure 4, together with those of the corresponding thiols. The IR spectrum of Cell-4ABT [Fig. 4(a)] had several strong peaks at the same positions as those of 4ABT [Fig. 4(b)]. The spectrum of Cell-MBA [Fig. 4(c)] showed a strong absorption at 1392 $cm^{-1}$ (carboxylate, $\nu_s$) and 1553 $cm^{-1}$ (carboxylate, $\nu_{as}$). Some other peaks were ascribed to aromatic $\nu_{C=C}$ (around 1600 $cm^{-1}$) and $\nu_{C=O}$ (1700 $cm^{-1}$) vibrations but the comprehensive as-

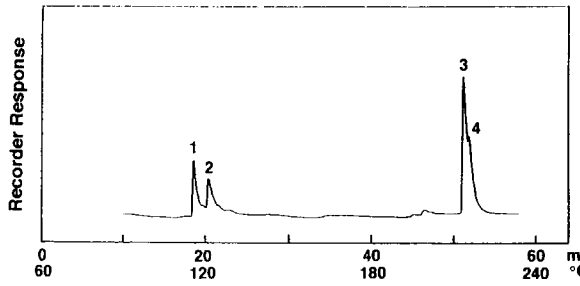



**Figure 6** GC chromatogram of MTFA derivative of hydrolyzate of Cell-4ABT ($DS_S$ = 0.79, $DS_{Br}$ = 0.02). Peak 1, α-Glc*p*; peak 2, β-Glc*p*; peaks 3 and 4, 4ABT-Glc.

signment was difficult even by comparison with the spectrum of MBA [Fig. 4(d)].

## $^{13}C$ NMR

Samples of Cell-MBA, Cell-CYS, and Cell-MBDA were soluble in alkaline solutions. Their $^{13}C$ NMR spectra were measured in alkaline $D_2O$ (Fig. 5). Signals of cellulose chain carbons were assigned based on the data measured in alkaline $D_2O$[17] and in LiCl–*N*-methyl-2-pyrrolidone.[18] Judging from the data for 6-deoxy-6-ethylthio-β-D-glucopyranose derivatives,[19] a signal of C-6 carbon bound to sulfur is expected to appear in 30–35 ppm, nearly the same region as that of C-6 carbon bound to bromine.[20] The $DS_{Br}$ values of the samples for NMR measurements were appreciably lower than their $DS_S$ values, and, therefore, signals in 34–37 ppm could be assigned to C-6 carbons bound to sulfur. Signals of carbons of thiol moieties were assigned based on the spectra of model compounds, *S*-ethylcysteine[5] for Cell-CYS and ethylthiobutanedioic acid[6] for Cell-MBDA. The assignments for the model compounds were based on 2-D $^1H$-$^1H$ and $^{13}C$-$^1H$ NMR measurements.

Carbons in the thiol moieties are more free for motion than carbons of rigid pyranose rings and give sharper peaks. As a consequence, the peak heights of the signals of the carbons in the thiol moieties relative to those of the ring carbons were higher than those expected from the $DS_S$ values.

The spectrum for Cell-MBDA was somewhat complicated [Fig. 5(a)]. Signals of carbons of thiol moieties of Cell-MBDA were assigned based on the spectra of model compounds, DL-2-*S*-ethylthiobutanedioic acid. The absorptions of C-6 and A carbons appeared as doublets. The reason for this is unknown at present, but it could be due to the effect of adjacent repeating units of different structures. The signal at 181.8 ppm, whose intensity relative to that of C-1

**Table V Mass Fragmentation Pattern of *N*, *O*-TFA Derivative of 4ABT-Glc**

| | Peak 3/Fig. 6 4ABT-Glc | |
|---|---|---|
| Assignment[a] | *m/z* | r.a.[b] |
| M | 767 | 97.1 |
| M—F | 748 | 1.1 |
| M—H—$CF_3$ | 697 | 2.6 |
| M—$CF_3CO$ | 670 | 3.6 |
| M—$CF_3COO$ | 654 | 0.2 |
| M—F—$CF_3COOH$ | 634 | 0.8 |
| M—$CF_3COO$—$CF_3CO$ | 557 | 1.7 |
| M—$CF_3COO$—$CF_3COOH$ | 540 | 0.9 |
| M—F—2$CF_3COOH$ | 520 | 0.9 |
| $A_3^2$ | 319 | 3.6 |
| $CH_2SC_6H_4NHCOCF_3$ | 234 | 100 |
| $SC_6H_4NHCOCF_3$ | 220 | 75.8 |
| $CH_2SC_6H_4NH$ | 137 | 43.1 |
| $CF_3$ | 69 | 53.2 |

[a] Nomenclature of fragment ions, see Refs. 2 and 23.
[b] Relative abundance, %.

carbon was much higher than those observed on the spectra of Cell-CYS and Cell-MBA [Fig. 5(b) and 5(c)], was assigned to the overlapping signals of two C=O carbons. The C=O carbon signals of DL-2-*S*-ethylthiobutanedioic acid appeared at positions very close to each other, 181.7 and 182.0 ppm.

The NMR spectrum of Cell-CYS is given in Figure 5(b). The signals on the spectrum for Cell-CYS were assigned based on the spectrum of *S*-ethyl-L-cysteine. The spectrum of Cell-CYS indicated that the mercapto group in cysteine was bound to cellulose at C-6, and the signals of C-6 carbon bound to the amino group in cysteine was not found. The signal of a C-6 carbon bound to nitrogen is expected to appear at 40 or higher ppm.[21]

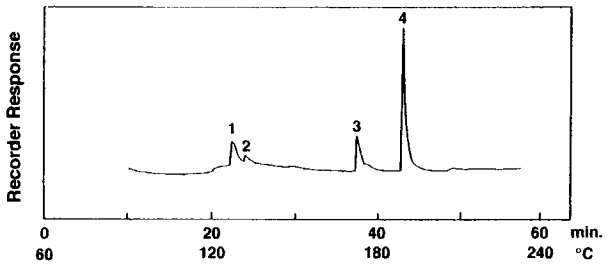



**Figure 7** GC chromatogram of MTFA derivative of hydrolyzate of Cell-MPA ($DS_S$ = 0.49, $DS_{Br}$ = 0.11). Peak 1, Me α-Glc; peak 2, SH-Glc; peak 3, MPA-Glc; peak 4, Me MPA-Glc.

The spectrum for Cell-MBA is given in Figure 5(c). The signal of C-6 carbons bound to sulfur appeared at 37.3 ppm. The signals of phenyl carbons appeared in 125–145 ppm.

## GC–MS

In the previous article,[1] the structures of the reaction products of halodeoxycelluloses with thiols were studied by GC and GC–MS analyses of the hydrolyzates of the reaction products after (*N*),*O*-trifluoroacetylation. The reaction products including Cell-MEt and Cell-AET, that did not contain carboxyl groups, gave (*N*),*O*-trifluoroacetyl (TFA) derivatives of the corresponding *S*-substituted 6-mercapto-6-deoxyglucoses.

GC–MS analysis of Cell-4ABT, which contained no carboxyl group, was made in a similar way. Figure 6 shows a GC chromatogram for Cell-4ABT. Mass spectrometric analysis showed that peaks 3 and 4 were those of anomeric *N,O*-TFA derivatives of 6-(4-aminophenylthio)-6-deoxyglucose (4ABT-Glc) (see Table V). 4ABT-Glc gave the molecular ion abundantly formed. Ring form of the TFA derivative of 4ABT-Glc could not be determined because characteristic fragment ions to distinguish pyranose and furanose ring forms were not found, as most of *S*-substituted 6-mercapto-6-deoxyglucoses reported in the previous work.[1] Figure 6 also shows the

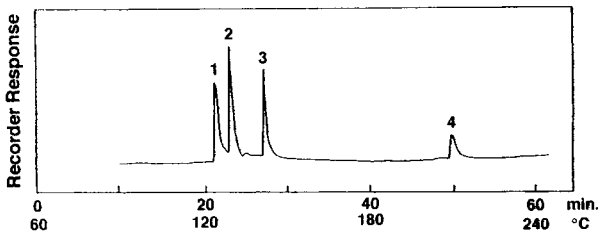



**Figure 8** GC chromatogram of MTFA derivative of hydrolyzate of Cell-MBDA ($DS_S$ = 0.47, $DS_{Br}$ = 0.24). Peak 1, Anh-Glc; peak 2, Me α-Glc; peak 3, Me Br-Glc; peak 4, Me MBDA-Glc.

anomeric peaks of glucopyranose (Glc*p*). No peak related to 6-(4-mercaptophenylamino)-6-deoxyglucose was found in the chromatogram, indicating that the amino function in 4ABT did not react with Cell-Br.

Reaction products of halodeoxycelluloses with carboxyl-containing thiols did not give volatile TFA derivatives of sulfur-containing glucose derivatives.[1] In some cases such as Cell-MPA, lactones of sulfur-containing glucose derivatives were formed as TFA derivatives, while in other cases, such as Cell-CYS, no volatile derivative was found in the chromatogram.[22] In the present study, four carboxyl-containing cellulose derivatives were studied by GC–MS after hydrolysis and two-step derivatization to methyl esters of TFA derivatives (MTFA derivatives). The

**Table VI Mass Fragmentation Patterns of 6-MPA-Glc and Me 6-MPA-Glc as MTFA Derivatives**

| | Peak 3/Fig. 7 MPA-Glc | | Peak 4/Fig. 7 Me MPA-Glc | |
|---|---|---|---|---|
| Assignment[a] | *m/z* | r.a.[b] | *m/z* | r.a.[b] |
| M | 666 | 2.6 | 584 | 8.4 |
| M — $OCH_3$ | 635 | 11.5 | 553 ($A_1$) | 12.2 |
| M — $COOCH_3$ | 607 | 31.3 | 525 | 6.4 |
| M — $CF_3COO$ | 553 ($A_1$) | 25.9 | 471 | n.d. |
| M — $CF_3COOH$ | 552 | 29.8 | 470 | n.d. |
| $A_1$ — $CF_3COOH$ | 439 ($A_2$) | 2.9 | 439 ($A_2$) | 2.5 |
| M — $CF_3COO$ — $2CF_3COOH$ | 325 | 2.7 | 243 | 2.0 |
| $A_2$ — $CH_2O$ | 409 | 18.2 | 409 | 18.2 |
| $C_3$ — H | 296 | 60.6 | 296 | 13.3 |
| $F_1$ | 271 | 75.9 | 271 | 13.4 |
| $CH_2SCH_2CH_2COOCH_3$ | 133 | 54.9 | 133 | 100 |
| $SCH_2CH_2COOCH_3$ | 119 | 92.3 | 119 | 62.1 |
| $CH_2CH_2COOCH_3$ | 87 | 49.3 | 87 | 31.6 |
| $CH_2COOCH_3$ | 73 | 13.7 | 73 | 13.1 |
| $CF_3$ | 69 | 100 | 69 | 65.7 |
| $COOCH_3$ | 59 | 51.2 | 59 | 39.2 |

[a] Nomenclature of fragment ions, see Refs. 2 and 23.
[b] Relative abundance, %.

**Table VII Mass Fragmentation Patterns of Me Br-Glc and Me MBDA-Glc as MTFA Derivatives**

| Assignment[a] | Peak 3/Fig. 8 Me Br-Glc | | Peak 4/Fig. 8 Me MBDA-Glc | |
|---|---|---|---|---|
| | *m/z* | r.a.[b] | *m/z* | r.a.[b] |
| M + 1 | 545 | 0.2 | 643 | 6.5 |
| M | 544[c] | 0.2 | 642 | 0.0 |
| M − 17 | 527 | n.d. | 625 | 3.0 |
| M − $OCH_3$ | 513[c] | 0.2 | 611 | 12.7 |
| M − $COOCH_3$ | 485 | n.d. | 583 | 6.3 |
| | | | 580.6[d] | 1.7 |
| M − 17 − $COOCH_3$ | 468 | n.d. | 565 | 2.6 |
| | | | 556.3[e] | 0.9 |
| M − Br | 465 | 0.3 | | |
| M − $OCH_3$ − $COOCH_3$ | 454 | n.d. | 551 | 5.2 |
| M − $CH_2Br$ | 451 | 0.4 | | |
| M − $CF_3COO$ | 431[c] | 2.3 | 529 | n.d. |
| M − Br − $HCOOCH_3$ | 405 | 28.8 | | |
| M − $COOCH_3$ − $HCOOCH_3$ | 423 | n.d. | 523 | 1.9 |
| M − $OCH_3$ − $CF_3COOH$ | 399[c] | 0.2 | 497 | 1.1 |
| M − $COOCH_3$ − $CF_3COOH$ | 371[c] | 7.9 | 469 | 6.5 |
| M − $OCH_3$ − $HCOOCH_3$ − $CF_3COOH$ | 339 | n.d. | 437 | 4.8 |
| $A_3^2$ | 319 | 2.8 | 319 | 3.3 |
| M − Br − $HCOOCH_3$ − $CF_3COOH$ | 291 | 20.7 | | |
| M − $OCH_3$ − $2CF_3COOH$ | 285[c] | 5.8 | 383 | 4.0 |
| $F_1$ | 265 | 25.0 | 265 | 3.3 |
| $H_1$ | 252 | 13.4 | 252 | n.d. |
| Not identified | 157 | 100 | 157 | 14.2 |
| $(CH_2COOCH_3)_2$ | | | 146 | 100 |
| 146 − $HOCH_3$ | | | 114 | 71.9 |
| $CF_3$ | 69 | 89.7 | 69 | 41.8 |
| $COOCH_3$ | 59 | 12.8 | 59 | 23.5 |

[a] Nomenclature of fragment ions, see Refs. 2 and 23.
[b] Relative abundance, %.
[c] Doublet.
[d] and [e] Metastable ions from *m/z* 643 to *m/z* 611 and from *m/z* 611 to *m/z* 583, respectively.

hydrolyzates were treated with HBr–methanol followed by trifluoroacetylation. Under the derivatization conditions used, parts of glucose derivatives were converted to methyl glucoside derivatives.

Figure 7 shows a GC chromatogram for Cell-MPA. In addition to a peak of methyl glucoside (Me Glc), several new peaks appeared on the chromatogram. The mass spectrometric analysis (see Table VI) showed that peaks 3 and 4 were those of MTFA derivatives of 6-(2-carboxyethylthio)-6-deoxyglucose (MPA-Glc) and that of the corresponding methyl glucoside (Me MPA-Glc). Both peak materials gave molecular ions and $A_1$ ions in appreciable amounts. The nomenclature of the fragment ions is based on Refs. 2 and 23. Fragment ions due to the elimination of $CH_3O$, $CH_3OCO$ and $CF_3COOH$, characteristic of MTFA derivatives, were all found. Sulfur-containing fragment ions are abundantly formed, which made the interpretation of the mass spectra easier. The lactone was not formed in the present case. Peak 2 was identified as an *O,S*-TFA derivative of 6-mercapto-6-deoxyglucose (SH-Glc).[24] The presence of this compound in the hydrolyzate shows that some of thioether linkages in MPA-Glc were cleaved during acid hydrolysis and/or the treatment with HBr–methanol.

Figure 8 shows a GC chromatogram for Cell-MBDA. Peak 4 was assigned to a MTFA derivative of methyl 6-(1,2-dicarboxyethylthio)-6-deoxyglucopyranoside (Me MBDA-Glc) by mass spectrometric analysis (see Table VII). Figure 8 shows peaks of TFA derivatives of 3,6-anhy-

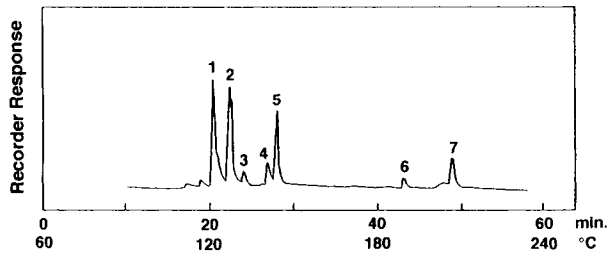



**Figure 9** GC chromatogram of MTFA derivative of hydrolyzate of Cell-CYS ($DS_S$ = 0.49, $DS_{Br}$ = 0.16). Peak 1, Anh-Glc; peak 2, Me α-Glc; peak 3, SH-Glc; peak 4, incompletely derivatized SH-Glc; peak 5, Me SH-Glc; peak 6, CYS-Glc; peak 7, Me CYS-Glc.

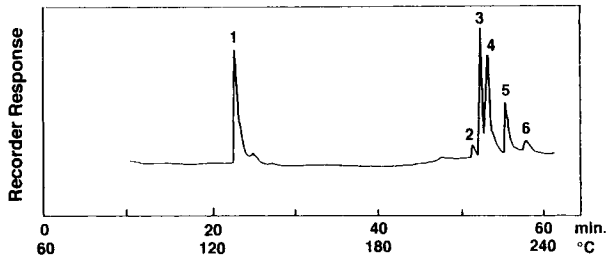



**Figure 10** GC chromatogram of MTFA derivative of hydrolyzate of Cell-MBA ($DS_S$ = 0.59, $DS_{Br}$ = 0.14). Peak 1, Me α-Glc; peaks 2 and 3, MBA-Glc; peaks 4, 5, and 6, see text and Scheme 2.

droglucose (Anh-Glc) and methyl 6-bromo-6-deoxyglucoside (Me Br-Glc) in addition to a TFA derivative of Me Glc. The sample of Cell-MBDA studied contained a relatively large amount of 6-bromo-6-deoxyglucose (Br-Glc) units ($DS_{Br}$, 0.24). Anh-Glc was formed in appreciable amounts along with Br-Glc when Cell-Br was hydrolyzed.[3] The peak area of Me MBDA-Glc shown in Figure 8 was, however, much smaller than the total peak area

**Table VIII Mass Fragmentation Patterns of Me SH-Glc, CYS-Glc, and Me CYS-Glc as MTFA Derivatives**

| | Peak 5/Fig. 9 Me SH-Glc | | Peak 6/Fig. 9 CYS-Glc | | Peak 7/Fig. 9 Me CYS-Glc | |
|---|---|---|---|---|---|---|
| Assignment[a] | *m/z* | r.a.[b] | *m/z* | r.a.[b] | *m/z* | r.a.[b] |
| M | 594 | 0.3 | 777 | 1.8 | 695 | 0.8 |
| MH—F | 576 | n.d. | 759 | 0.7 | 677 | 0.9 |
| M—$OCH_3$ | 563 | 0.6 | 746 | n.d. | 664 | 2.5 |
| M—$COOCH_3$ | 535 | 2.7 | 718 | 2.3 | 636 | 0.5 |
| M—$OCH_3$—$HCOOCH_3$ | 503 | n.d. | 686 | n.d. | 604 | 8.7 |
| M—$CF_3COO$ | 481 | 2.3 | 664 | 31.7 | 582 | 74.9 |
| M—$OCH_3$—$CF_3COOH$ | 449 | n.d. | 632 | 1.6 | 550 | 9.2 |
| M—$CF_3COO$—$HCOOCH_3$ | 421 | 11.0 | 604 | 3.1 | 522 | 11.8 |
| M—$OCH_3$—$CF_3COOH$—$HCOOCH_3$ | 389 | n.d. | 572 | n.d. | 490 | 5.0 |
| Not identified | | | 593 | 5.4 | 593 | 1.3 |
| M—$CF_3COO$—$CF_3COOH$ | 367 | 2.8 | 550 | 70.2 | 468 | 0.6 |
| M—$OCH_3$—$NH_2COCF_3$—$CF_3COOH$ | | | 519 | n.d. | 436 | 22.8 |
| M—$CF_3COO$—$2CF_3COOH$ | 253 | 8.1 | 436 | 5.4 | 354 | 4.0 |
| Not identified | | | 407 | 12.6 | 407 | 14.1 |
| M—$SCOCF_3$—$HCOOCH_3$ | 405 | 9.3 | | | | |
| $A_3^2$ | 319 | 3.3 | 319 | 22.1 | 319 | 6.8 |
| 405—$CF_3COOH$ | 291 | 26.4 | 291 | 5.1 | 291 | 5.1 |
| $F_1$—$NH_2COCF_3$ | | | 269 | 16.4 | 269 | 8.8 |
| $SCH_2CH(NHCOCF_3)COOCH_3$ | | | 230 | 16.2 | 230 | 16.1 |
| $CH_2CH(NHCOCF_3)COOCH_3$ | | | 198 | 28.2 | 198 | 41.2 |
| $CH(NHCOCF_3)COOCH_3$ | | | 184 | 19.0 | 184 | 45.8 |
| $SCH{=}CHCOOCH_3$ | | | 117 | 53.8 | 117 | 72.9 |
| $COCF_3$ | 97 | 24.4 | 97 | 28.2 | 97 | 27.8 |
| $CF_3$ | 69 | 100 | 69 | 100 | 69 | 100 |
| $COOCH_3$ | 59 | 17.0 | 59 | 25.8 | 59 | 33.3 |

[a] Nomenclature of fragment ions, see Refs. 2 and 23.
[b] Relative abundance, %.

**Table IX Mass Fragmentation Patterns of MTFA Derivatives of Me MBA-Glc and TFA Derivatives of Related Lactones**

| | Peak 3/Fig. 10 Me MBA-Glc | | Peak 4/Fig. 10 Lactone | | Peak 6/Fig. 10 Lactone | |
|---|---|---|---|---|---|---|
| Assigment[a] | *m/z* | r.a.[b] | *m/z* | r.a.[b] | *m/z* | r.a.[b] |
| M | 632 | 24.2 | 504 | 26.6 | 504 | 31.2 |
| M—18 | 614 | 1.2 | 486 | n.d. | 486 | n.d. |
| M—$OCH_3$ | 601 | 1.8 | 473 | 2.7 | 473 | 2.5 |
| | 596.5[c] | 1.3 | | | | |
| M—61 | 571 | 0.8 | 443 | 0.6 | 443 | n.d. |
| M—$CF_3COO$ | 519 | 0.2 | 391 | 0.2 | 391 | n.d. |
| M—$OCH_3$—$CF_3COOH$ | 487 | 3.6 | 359 | n.d. | 359 | n.d. |
| M—$2OCH_3$—$CF_3COOH$ | 457 | 4.4 | 329 | n.d. | 329 | n.d. |
| M—$COOCF_3$—$CF_3COOH$ | 405 | n.d. | 277 | 1.8 | 277 | 4.4 |
| M—$OCH_3$—$2CF_3COOH$ | 373 | 1.1 | 245 | | 245 | n.d. |
| $A_3^2$ | 319 | 8.6 | 319 | 2.8 | 319 | 2.7 |
| (see Scheme 2) | 179 | 3.1 | 179 | 6.3 | 179 | 100 |
| 179–28 | 151 | 13.5 | 151 | 8.6 | 151 | 56.7 |
| 179–28–14 | 137 | 15.0 | 137 | 18.4 | 137 | 73.3 |
| | 183 | 38.5 | 183 | 6.4 | 183 | 18.2 |
| $CH_2SC_6H_4COOCH_3$ | 181 | 50.9 | 181 | 2.7 | 181 | 13.0 |
| $SC_6H_4COOCH_3$ | 167 | 100 | 167 | 16.6 | 167 | 20.0 |
| (see Scheme 2) | 136 | 32.2 | 136 | 100 | 136 | 73.3 |
| $C_6H_4S$ | 108 | 14.1 | 108 | 8.6 | 108 | 2.9 |
| | 73 | 9.0 | 73 | 6.3 | 73 | 63.3 |
| $CF_3$ | 69 | 40.8 | 69 | 31.5 | 69 | 74.7 |

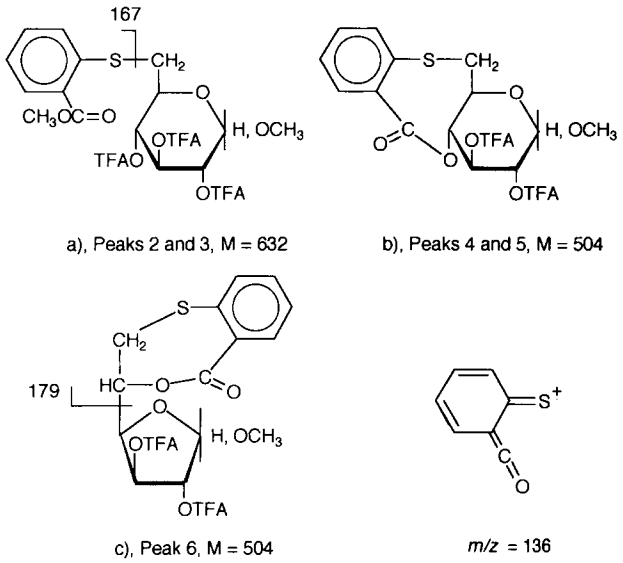
[a] Nomenclature of fragment ions, see Refs. 2 and 23.
[b] Relative abundance, %.
[c] Metastable ion from *m/z* 632 to *m/z* 614.

of Me Glc, Me 6-Br-Glc, and Anh-Glc, although $DS_S$ was as high as 0.47. This suggests that a considerable amount of 6-(1,2-dicarboxyethylthio)-6-deoxyglucose (MBDA-Glc) units in Cell-MBDA was degraded, probably to Glc and/or Anh-Glc during the hydrolysis of the sample and/or the derivatization with HBr–methanol. The mass fragmentation pattern of a TFA derivative of Me Br-Glc is given in Table VII.

Figure 9 shows a GC chromatogram of Cell-CYS. Mass spectrometric analysis (Table VIII) indicated that peaks 6 and 7 were those of MTFA derivatives of 6-(2-amino-2-carboxyethylthio)-6-deoxyglucose (CYS-Glc) and the corresponding methyl glucoside (Me CYS-Glc). Figure 9 also gives relatively large peaks of TFA derivatives of Me Glc, Anh-Glc, and methyl 6-mercapto-6-deoxyglucoside (Me SH-Glc) in addition to a small peak of a TFA derivative of SH-Glc. Here, again, a part of CYS-Glc units in Cell-CYS was degraded, probably to Glc, Anh-Glc, and/or SH-Glc during the hydrolysis and/or the derivatization. The mass fragmentation pattern of a TFA derivative of Me SH-Glc is given in Table VIII. No peak related to 6-(1-carboxy-2-mercaptoethylamino)-6-deoxyglucose was found in the chromatogram, indicating that the amino group in CYS did not react with Cell-Br under the conditions studied.

All three aliphatic carboxyl-containing cellulose derivatives, Cell-MPA, Cell-MBDA, and Cell-CYS, gave peaks of the corresponding sulfur-containing methyl glucosides as MTFA derivatives as described above, confirming that the nucleophilic substitution reactions of thiols with Cell-Br took place. Cell-MPA and Cell-CYS also gave smaller peaks of the corresponding sulfur-containing glucoses, which eluted at lower temperatures than the eluting temperatures of the corresponding methyl glucosides.

Figure 10 shows GC chromatogram for Cell-MBA. Five new peaks appeared in the chromatogram. Peaks 2 and 3 were assigned to MTFA derivatives of methyl 6-(2-carboxyphenylthio)-6-deoxyglucoside (Me MBA-Glc). No peak was found for the corresponding glucose derivative, and instead, three




**Scheme 2**

peaks of TFA derivatives of lactones of Me MBA-Glc were identified by mass spectrometry (Table IX). Two of the three peaks (peaks 4 and 5) were anomeric peaks of the lactone in pyranose form and peak 6 was that in furanose form. The structures of the compounds mentioned above are given in Scheme 2, where Me MBA-Glc assumes the pyranose form. All the compounds gave molecular ions and the ion of m/z 136 (see Scheme 2) abundantly.

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