ELSEVIER

0144-8617(95)00027-5

Carbohydrate Polymers 27 (1995) 13–21

0144-8617/95/$09.50+.00

Gas chromatographic–mass spectrometric study of reactions of halodeoxycelluloses with thiols in aqueous solutions

Nobuyoshi Aoki, Katsuya Koganei, Hu-Sheng Chang, Ken-ichi Furuhata & Munenori Sakamoto*

Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152, Japan

(Received 19 January 1995; revised version received 21 February 1995; accepted 8 March 1995)

Chloro- and bromodeoxycelluloses with high degrees of substitution, prepared with halosuccinimide and triphenylphosphine under homogeneous conditions, were treated with eight thiols under moderately alkaline conditions. Bromodeoxycellulose was generally more reactive than chlorodeoxycellulose and carboxyl-bearing thiols such as mercaptoacetic acid were less reactive than neutral thiols such as benzenethiol. The maximum conversion of halodeoxyglucose units to thio derivatives was 65%. When the reaction was run at high alkalinity at 60°C, elimination of hydrogen halide to yield 3,6-anhydroglucose and/or 5,6-glucosene units took place appreciably as a side reaction. Hydrolysates of the reaction products with thiols having no carboxyl group were analyzed by gas chromatography–mass spectrometry as trifluoroacetates and the formation of *S*-substituted 6-thio-6-deoxyglucose units was confirmed.

INTRODUCTION

We have reported facile syntheses of chlorodeoxycellulose and bromodeoxycellulose at high degrees of substitution by halogen under homogeneous conditions with *N*-halosuccinimide and triphenylphosphine (Furuhata *et al.*, 1992*a*, 1992*c*) and studied the nucleophilic substitution reactions of such halodeoxycelluloses with inorganic ions (Furuhata *et al.*, 1992*b*). In this paper, we report nucleophilic substitution reactions between halodeoxycelluloses and various thiols in aqueous alkaline solutions under heterogeneous conditions. Thiols are expected to be more nucleophilic under alkaline conditions.

Vigo and Welch (1970) reported reactions of various thiols with chlorodeoxycellulose which was prepared by treating cotton with thionyl chloride under heterogeneous conditions. The chlorodeoxycellulose used in their study had a low chlorine content (Cl, 4·7%) and contained 0·6% of sulfur as sulfite ester.

In most experiments in the present study, we used chlorodeoxycellulose with a degree of substitution (*DS*) by chlorine between 0·9 and 1·0 and bromodeoxycellulose with *DS* by bromine between 0·6 and 0·8. The chlorodeoxycellulose of such a high *DS* mainly consists of 6-chloro-6-deoxyglucose (1) units and some 3,6-dichloro-3,6-dideoxyallose (2) units. The bromodeoxycellulose used consists of 6-bromo-6-deoxyglucose (3) units and some unmodified glucose units. The reaction of halodeoxycellulose with thiols bearing less reactive functional groups will provide a method to introduce such functional groups to cellulose through thioether bridges.

*To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Microcrystalline cellulose (Art 2331 cellulose mikrokristallin, Merck®) was dried under reduced pressure before use. *N*,*N*-Dimethylacetamide (DMA) was dried with calcium hydride and distilled under reduced pressure. Commercial thiols were used without further purification.

Halogenation of cellulose

Microcrystalline cellulose was halogenated according to the methods previously reported (Furuhata *et al.*, 1992*a*, 1992*c*). Halogenated samples were recovered by pouring the reaction solutions into an excess amount of acetone, washed with acetone and methanol several times until the washing became colorless and then treated with a sodium carbonate solution (pH 11·5) overnight. The halogenated samples were dialysed against running water and distilled water for 3 days each, and dried under reduced pressure before analyses and further reactions.

Reaction with thiols

The nucleophilic substitution with a thiol was carried out in aqueous sodium hydroxide. A mixture of halodeoxycellulose sample and a thiol was stirred in the solution at a prescribed temperature. After the reaction, the sample was washed with water and methanol, and dried under reduced pressure before analyses. The product with benzenethiol was washed with ethanol before drying. In the case of the reaction with carboxyl-bearing thiols under relatively strong alkaline conditions, the reaction mixture was dialysed against distilled water for 3 days. The solution in the dialysis tube was freeze-dried to collect materials remaining dissolved after centrifugation. The reaction mixture with cysteine was dialysed against aqueous sodium carbonate solution (pH 11·5) for 3 days before dialysis against distilled water.

Analyses

Halogen and sulfur contents were determined simultaneously via an oxygen flask combustion method (Kinoshita & Hozumi, 1965). The degree of substitution of the sample was determined by elemental analyses of halogen and sulfur. Infrared spectra of the samples were recorded in KBr discs on a Fourier-transform infrared spectrophotometer FT/IR-3 (Nihon Bunko Co.).

The chemical structure of a sample was studied by gas chromatography (GC) and gas chromatography mass spectrometry (GC–MS) after hydrolysis. The sample for analysis was hydrolysed with sulfuric acid (Furuhata *et al.*, 1992*a*) in a way similar to that (Rowland *et al.*, 1966) adopted for the analysis of various cellulose derivatives. A sample (10 mg) was soaked in 2 ml of 72% sulfuric acid at 5 °C until dissolution. Distilled water (25 ml) was added to the solution and the solution was refluxed for 4 h. The hydrolysate solution was neutralized with barium carbonate. The barium sulfate was removed by centrifugation and the supernatant was evaporated. The residue was transferred into a Reacti-Vial and converted into trifluoroacetate (Furuhata *et al.*, 1992*a*). A GC 4BMP gas chromatograph (Shimadzu Corp.) equipped with two flame-ionization detectors was used for GC analysis. The stationary phase used was SE-30 on Gas Chrom Q (100–120 mesh, 3 wt%). A Shimadzu LKB-9000 gas chromograph-mass spectrometer was used for GC–MS analysis. The operation conditions for GC and GC–MS instruments were the same as those previously described (Furuhata *et al.*, 1992*a*).

RESULTS AND DISCUSSION

Reactions of halodeoxycellulose with thiols

Reactions of chlorodeoxycellulose and bromodeoxycellulose with eight thiols were run mostly in aqueous alkaline solutions. Among the thiols used were three neutral thiols: methanethiol, benzenethiol, and 2-mercaptoethanol; an amino-bearing thiol: 2-aminoethanethiol; three carboxy-bearing thiols: mercaptoacetic acid, 3-mercaptopropanoic acid and 2-mercaptobenzoic acid; and an amino acid: cysteine.

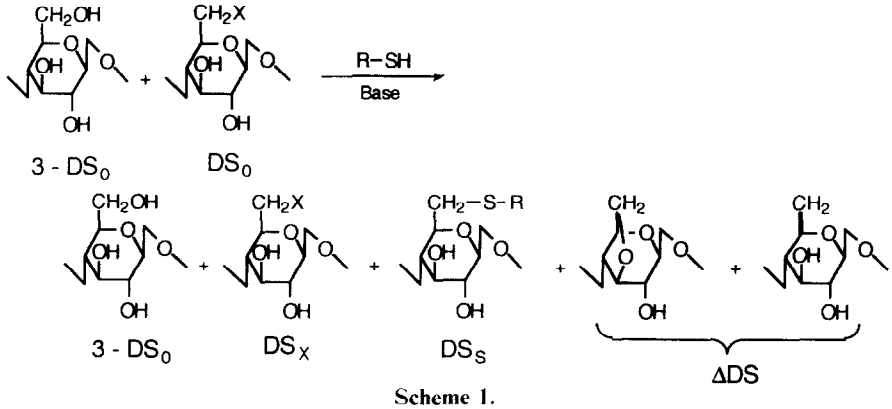
The sulfur (S, %) and halogen (X, %) contents of the reaction product were determined after purification by dialysis and drying. The degree of substitution by thiol (DS_S) and that by remaining halogen (DS_X) of a sample were calculated by

$$DS_S = \frac{M_S \times (162{\cdot}14 - 18{\cdot}015 \times DS_0) \times S}{C} \quad (1)$$

$$DS_X = \frac{M_X \times (162{\cdot}14 - 18{\cdot}015 \times DS_0) \times X}{C} \quad (2)$$

$$C = \{(M_X + 1{\cdot}008) \times M_S \times X - M_X(M_T \times S - 100 \times M_S)\} \quad (3)$$

where M_X, M_S, M_T and DS_0 are atomic weight of halogen and sulfur, molecular weight of the thiol used, and the degree of substitution by halogen of the original halodeoxycellulose, respectively. Possible loss of intramolecular hydrogen halide under alkaline conditions (Furuhata *et al.*, 1992*c*) due to the formation of 3,6-anhydroglucose (4) and/or 5,6-glucosene (5) units was taken into account in the above calculation. A simplified reaction scheme is given below.



Scheme 1.

The extent of such a side reaction is estimated by

$$\Delta DS = DS_0 - (DS_S + DS_X) \quad (4)$$

and the conversion (%) of halogen in halodeoxycellulose to the sulfur derivative is $100 \times DS_S/DS_0$.

Table 1 summarizes the reactions of chlorodeoxycellulose with thiols. The three neutral thiols reacted with chlorodeoxycellulose in high conversions (32–64%). The side reaction yielding (4) and/or (5) did not take place appreciably when the reaction was run at an alkali concentration $\leqslant$0·3 N. The reactions of methanethiol were run under strong alkaline conditions because high concentrations of sodium mercaptide of methanethiol were used as a reagent and the intramolecular loss of hydrogen chloride occurred as a side reaction in this case. 2-Aminoethanethiol reacted with chlorodeoxycellulose in high conversions (up to 53%) under appropriate conditions. As in the case of methanethiol, the intramolecular dehydrochlorination took place at appreciable levels when a high concentration of 2-aminoethanethiol was used.

All three carboxyl-bearing thiols and cysteine did not react significantly when the concentration of added alkali was lower than the concentration of the thiol. When a moderate excess of alkali was used for the reaction of mercaptoacetic acid (Expt 12), conversion was improved to 34%. When a great excess of alkali was used for the reaction of 3-mercaptopropanoic acid (Expt 15), the yield was very low and the product showed a low conversion with a very high ΔDS value. The soluble fraction of the product was recovered from solution in the dialysis tube. This fraction showed a slightly higher conversion but again with a high ΔDS.

Table 2 summarizes the reactions of bromodeoxycellulose with thiols. The reaction conditions used were generally milder than those used for the reactions of chlorodeoxycellulose. Most of the reactions were studied at 45°C. The reactions of three neutral thiols and amino-bearing 2-aminoethanethiol took place at high conversions (40–70%). Although the reaction conditions were milder, the conversions of bromodeoxycellulose with methanethiol and benzenethiol were considerably higher than those of chlorodeoxycellulose, respectively, indicating the higher reactivity of bromodeoxycellulose than chlorodeoxycellulose. The alkalinity of the reaction system for the reaction of bromodeoxycellulose with methanethiol was equal to that for the reaction of chlorodeoxycellulose with methanethiol. However, the ΔDS value for the reaction of bromodeoxycellulose was lower than that observed for the corresponding reaction of chlorodeoxycellulose, probably due to the difference in reaction temperature.

The conversion and the ΔDS remained low (conversion, 14–16%; ΔDS, 0·06–0·08) when bromodeoxycellulose was treated with mercaptoacetic acid or 3-mercaptopropanoic acid with a slight excess of alkali at 45°C (Expts 23 and 25). The conversion was still low when the reaction with mercaptoacetic acid was run at 60°C with a slight excess of alkali (Expt 24) but the yield of the product dropped and the ΔDS became very high. When the reaction of bromodeoxycellulose with 3-mercaptopropanoic acid was run with an equimolar amount of added alkali at 60°C (Expt 26), the conversion was improved to 39% without a significant increase in the ΔDS. A small amount of the soluble fraction of the product was recovered, which showed a much higher conversion. On the other hand, when the reaction was carried out with an excess amount of alkali also at 60°C (Expt 27), both insoluble and soluble fractions of the reaction product showed high ΔDS values. 2-Mercaptobenzoic acid failed to react significantly with chlorodeoxycellulose at 60°C as mentioned earlier but it reacted much more with bromodeoxycellulose with a conversion of 23% at the same temperature without an increase in the ΔDS. The reaction of bromodeoxycellulose with cysteine did not proceed significantly as in the case of chlorodeoxycellulose.

IR spectra of some reaction products obtained from chlorodeoxycellulose are given in Fig. 1 along with that of chlorodeoxycellulose. The spectrum of the reaction product with benzenethiol shows several aromatic peaks. The spectrum of the product from 2-aminoethanethiol shows a peak of NH_3^+ at 1585 cm^{-1} and a shoulder in the 2500–3500 cm^{-1} region. The spectrum of the product from mercaptoacetic acid shows a peak at 1575 cm^{-1} (COO^-). The spectrum of the product from 3-mercaptopropanoic acid, taken after treating with a dilute hydrochloric acid, shows peaks at 1575 (COO^-) and 1730 cm^{-1} (COOH). The spectrum differs greatly from the others especially around the 1100 cm^{-1} region and similar to that reported for bromodeoxycellulose after an alkaline treatment (Furuhata *et al.*, 1992*c*). This indicates the formation of unit (4) during the treatment with 3-mercaptopropanoic acid under alkaline conditions. The spectrum of the product from cysteine shows a peak at 1635 cm^{-1} indicating the presence of $NH_3^+$and COO^-. The reaction products with methanethiol or 2-mercaptoethanol are not expected to give characteristic peaks. The spectrum of the reaction product with 2-mercaptobenzoic acid does not show the aromatic peaks because the extent of chemical modification was low. All samples show absorptions at 721 and 755 cm^{-1} due to the presence of unmodified C-Cl bonds. These IR data are consistent with the analytical data shown in Table 1. IR spectra of the reaction products from bromodeoxycellulose show new peaks as do the spectra for the reaction products from chlorodeoxycellulose.

GC and GC–MS analyses

In order to confirm the structures of the reaction products with thiols, the reaction products were acid hydrolysed, derivatized into trifluoroacetates (*O*-TFA derivatives) and analyzed by GC and GC–MS as

Table 1. Reactions of Cell-Cl with various thiols

No.	Thiol	[SH] mol/l	SH/Cl mol/mol	Added NaOH N	Other conditions	DS_0	Products				
							Yield (%)	DS_S	DS_X	Conv. (%)	ΔDS
1	Methanethiol	0·6[a]	20	0·0	B, E	1·01	25·4	0·40	0·39	40	0·22
2		7·4[a]	130	0·0	A, E	1·01	60·7	0·32	0·45	32	0·24
3	Benzenethiol	1·0	20	0·3	A, E	0·92	—	0·40	0·60	43	−0·08
4	Mercaptoethanol	0·6	20	0·2	B, E	1·01	60·3	0·36	0·57	36	0·08
5		1·0	20	0·3	A, E	0·92	—	0·59	0·40	64	−0·07
6	2-aminoethanethiol	0·1[b]	4·6	0·2	B, C	0·77	—	0·05	0·76	6	−0·03
7		0·2[b]	7·2	0·2	B, D	0·73	—	0·20	0·56	27	−0·03
8		0·3[b]	14	0·2	B, E	0·74	—	0·24	0·46	32	0·04
9		0·6	20	0·2	B, E	1·01	34·5	0·54	0·35	53	0·12
10		1·1	20	0·2	A, E	1·01	80·4	0·43	0·40	43	0·18
11	Mercaptoacetic acid	0·6	20	0·2	B, E	1·01	42·1	0·06	0·83	6	0·12
12		1·0	20	1·3	A, E	0·92	—	0·31	0·63	34	−0·02
13	3-mercaptopropanoic acid	0·6	20	0·2	B, E	1·01	89·2	0·02	0·96	2	0·03
14		0·6	20	0·6	B, E	1·01	53·9	0·09	0·90	9	0·02
15		0·5	18	1·3	B, E	1·01	6·8	0·12	0·06	12	0·83
							7·3[c]	0·22	0·18	22	0·61
16	Mercaptobenzoic acid	0·6	20	0·2	B, E	1·01	76·1	0·05	0·92	5	0·04
17	L-cysteine	0·6	20	0·2	B, E	1·01	21·6	0·17	0·80	17	0·03

A, Bath ratio 100; B, Bath ratio 200; C, 2 h at 45°C; D, 24 h at 60°C; E, 48 h at 60°C.
[a] Used as sodium mercaptide.
[b] Used as HCl salt.
[c] Soluble fraction during dialysis.

Table 2. Reactions of Cell-Br with various thiols

No.	Thiol	[SH] mol/l	SH/Br mol/mol	Added NaOH N	Other conditions[a]	DS_0	Products				
							Yield (%)	DS_S	DS_X	Conv. (%)	ΔDS
18	Methanethiol	0·5[b]	23	0·1	B	0·79	71·4	0·55	0·17	70	0·10
19	Benzenethiol	0·1	5·9	0·1	A	0·70	87·5	0·36	0·43	51	−0·09
20		0·1	5·9	0·2	A	0·60	70·1	0·41	0·30	68	−0·10
21	Mercaptoethanol	0·1	5·9	0·1	A	0·70	90·2	0·28	0·36	40	0·06
22	2-aminoethanethiol	0·1	5·9	0·2	A	0·60	62·7	0·28	0·07	47	0·25
23	Mercaptoacetic acid	0·1	5·9	0·2	A	0·70	78·8	0·10	0·54	14	0·06
24		0·5	30·5	0·7	C	0·79	33·9	0·03	0·02	4	0·74
25	3-mercaptopropanoic	0·1	5·9	0·2	A	0·70	91·1	0·11	0·51	16	0·08
26		0·6	32	0·6	C	0·79	64·0	0·31	0·40	39	0·08
							7·3[c]	0·58	0·43	73	−0·22
27		0·5	29	1·3	C	0·79	8·7	0·21	0·09	27	0·49
							16·4[c]	0·31	0·05	39	0·42
28	Mercaptobenzoic acid	0·1	5·9	0·2	A	0·70	88·7	0·16	0·50	23	0·04
29	L-cysteine[d]	0·1	5·9	0·2	A	0·70	79·7	0·12	0·65	17	−0·07

[a] Bath ratio was fixed to 200. A, 24 h at 45°C; B, 46 h at 45°C; C, 48 h at 60°C..
[b] Used as sodium mercaptide.
[c] Soluble fraction during dialysis.
[d] Used as HCl salt.

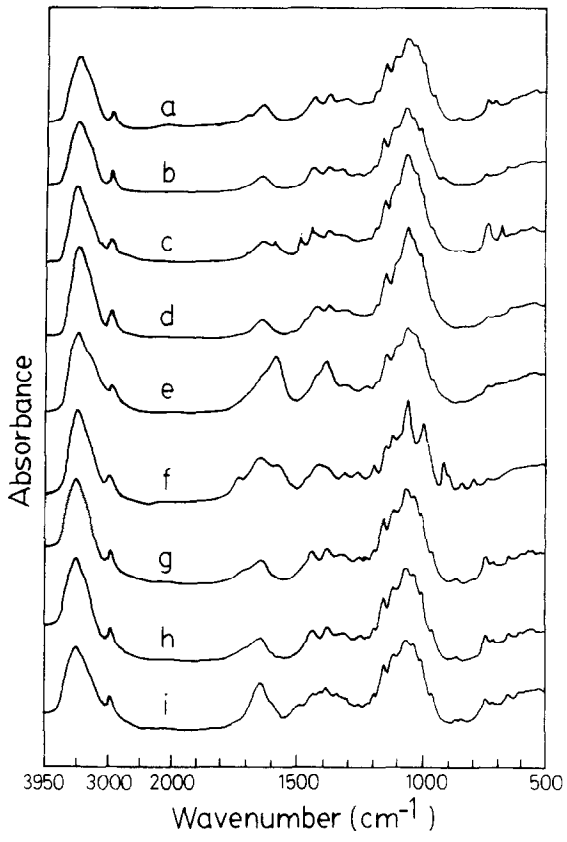


Fig. 1. IR spectra of chlorodeoxycellulose treated with various thiols: (a) chlorodeoxycellulose, *DS* 0·92; (b) methanethiol, DS_{Cl} 0·39, DS_S 0·40; (c) benzenethiol, DS_{Cl} 0·60, DS_S 0·40; (d) 2-mercaptoethanol, DS_{Cl} 0·40, DS_S 0·59; (e) mercaptoacetic acid DS_{Cl} 0·63, DS_S 0·31; (f) 3-mercaptopropanoic acid, DS_{Cl} 0·18, DS_S 0·22; (g) 2-mercaptobenzoic acid, DS_{Cl} 0·92, DS_S 0·05; (h) 2-aminoethanethiol, DS_{Cl} 0·46, DS_S 0·24; (i) cysteine, DS_{Cl} 0·80, DS_S 0·17.

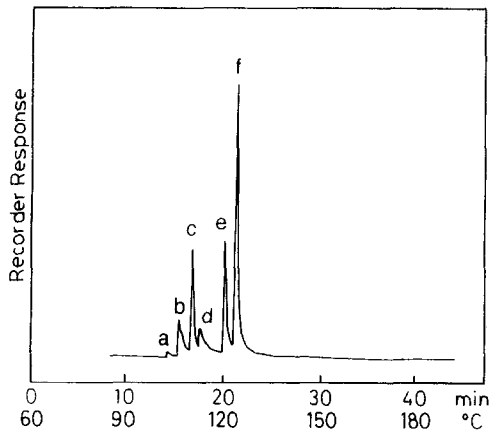


Fig. 2. GC chromatogram for TFA derivatives of hydrolysate of chlorodeoxycellulose treated with methanethiol in water at 60 C for 48 h (DS_{Cl}, 0·39, DS_S, 0·40). Peak a, α-D-glucopyranose; peak b, β-D-glucopyranose and 6-chloro-6-deoxyglucopyranose; peak c, 6-chloro-6-deoxyglucopyranose; peak d, 3,6-anhydroglucose; peaks e and f, compound 6.

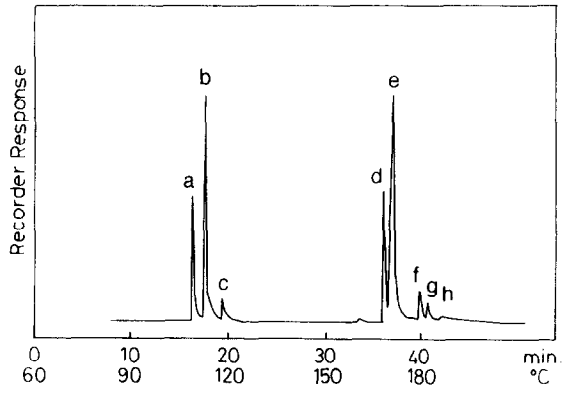


Fig. 3. GC chromatogram for TFA derivatives of hydrolysate of chlorodeoxycellulose treated with benzenethiol in 0·3 N NaOH at 60°C for 48 h (DS_{Cl}, 0·60, DS_S, 0·40). Peak a, β-D-glucopyranose and 6-chloro-6-deoxyglucopyranose; peak b, 6-chloro-6-deoxyglucopyranose; peak c, 3,6-dichloro-3,6-dideoxyallopyranose; peaks d and e, compound 7; peaks f, g and h were tentatively ascribed to compound 8.

reported previously (Furuhata *et al.*, 1992*a*). Gas chromatograms for the products obtained with methanethiol, benzenethiol, 2-mercaptoethanol, 2-aminoethanethiol and 3-mercaptopropanoic acid are shown in Figs 2–6 and mass fragmentation patterns of the well characterized peaks are summarized in Table 3. It is possible that some of thioether linkages are cleaved during acid hydrolysis, however, no product related to such cleavage was obtained in this work.

Figure 2 shows the GC chromatogram for the hydrolysate of chlorodeoxycellulose treated with methanethiol. Peaks a, b and c were TFA derivatives of glucose and (1), present in the starting chlorodeoxycellulose. Peak d was that of (4). Compound (4) has been often found in the chromatogram for the hydrolysates of bromodeoxycellulose and is considered to be an artefact formed from (3) in the hydrolysate during neutralization (Furuhata *et al.*, 1992*c*). However, this compound has never been found in the chromatogram for the hydrolysates of chlorodeoxycellulose (Furuhata *et al.*, 1992*a*). The presence of peak d probably indicates that the compound was not formed during finishing treatments but that the sample contained the unit of (4) in the molecular chain. The ΔDS value of this particular sample was relatively high as mentioned earlier. GC–MS analysis indicated that peaks e and f were TFA derivatives of 6-methylthio-6-deoxyglucose (6) (possibly a pair of anomers in pyranose form). The mass spectrometric data of the two peaks shown in Table 3 are essentially the same (Table 3).

Figure 3 shows the GC chromatogram for the hydrolysate of chlorodeoxycellulose treated with benzenethiol. GC-MS analysis showed that peaks d and e were TFA derivatives of 6-phenylthio-6-deoxyglucose (7). The mass fragmentation pattern is given in Table 3. Peaks f, g and h were tentatively assigned to those of 3-chloro-6-phenylthio-3,6-dideoxyallose (8) (Table 4).

Figure 4 shows the GC chromatogram for the hydro-

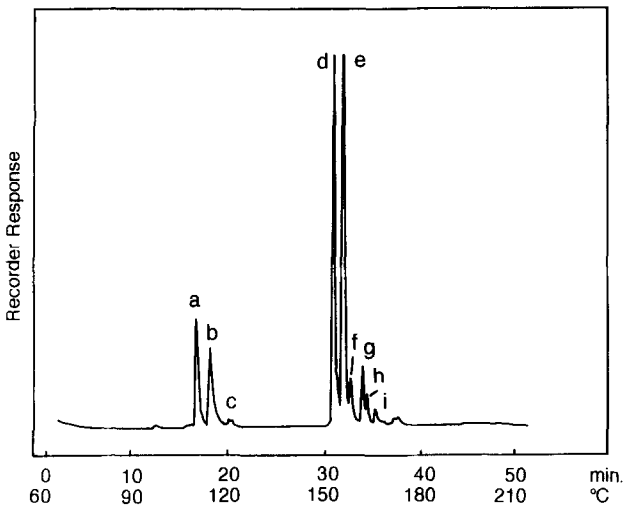


Fig. 4. GC chromatogram for TFA derivatives of hydrolysate of chlorodeoxycellulose treated with 2-mercaptoethanol in 0·2 N NaOH at 60°C for 48 h (DS_{Cl}, 0·40, DS_S, 0·59). Peak a, α-D-glucopyranose; peak b, β-D-glucopyranose and 6-chloro-6-deoxyglucopyranose; peak c, 3,6-dichloro-3,6-dideoxyallopyranose; peaks d, e and f, compound 9; peaks g, h and i were tentatively ascribed to compound 10.

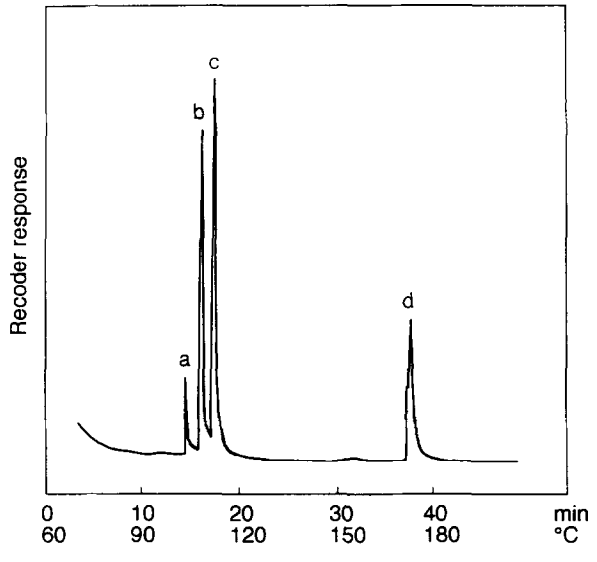


Fig. 5. GC chromatogram for TFA derivatives of hydrolysate of chlorodeoxycellulose treated with 2-aminoethanethiol in 0·2 N NaOH at 60°C for 48 h (DS_{Cl}, 0·46, DS_S, 0·24). Peak a, α-D-glucopyranose; peak b, β-D-glucopyranose and 6-chloro-6-deoxyglucopyranose; peak c, 6-chloro-6-deoxyglucopyranose; peak d, compound 11.

lysate of chlorodeoxycellulose treated with 2-mercaptoethanol. Peaks d–f were TFA derivatives of 6-(2-hydroxyethylthio)-6-deoxyglucose (9). Peaks g, h and i were tentatively assigned to those of 3-chloro-6-(2-hydroxyethylthio)-3,6-dideoxyallose (10) (Table 4). Figure 5 shows the GC chromatogram for the hydrolysate of chlorodeoxycellulose treated with 2-aminoethanethiol. Peak d was assigned to *N*-trifluoroacetyl trifluoroacetate of 6-(2-aminoethylthio)-6-deoxyglucose

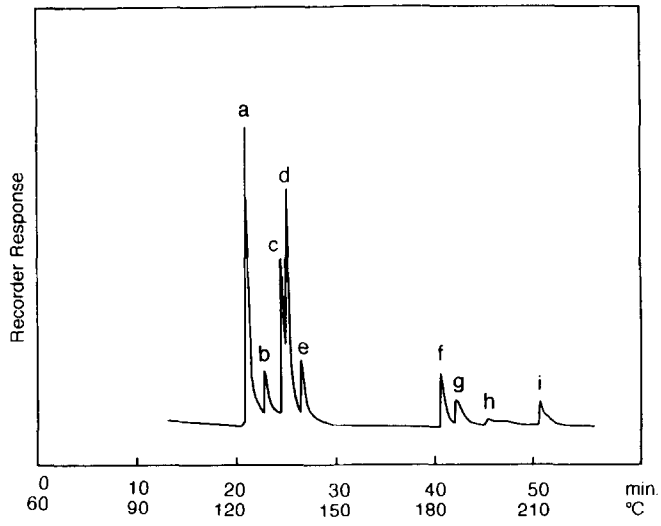


Fig. 6. GC chromatogram for TFA derivatives of hydrolysate of bromodeoxycellulose treated with 3-mercaptopropanoic acid in 0·6 N NaOH at 60°C for 48 h (DS_{Br}, 0·40, DS_S, 0·31). Peak a, α-D-glucopyranose; peak b, β-D-glucopyranose; peak c, 3,6-anhydroglucose; peaks d and e, anomers of 6-bromo-6-deoxyglucopyranose; peaks f and g were tentatively ascribed to compound 12; peak h, 4-*O*-(6-bromo-6-deoxy-β-D-glucopyranosyl)-D-glucopyranose; peak i, 4-*O*-(6-bromo-6-deoxy-β-D-glucopyranosyl)-6-bromo-6-deoxy-D-glucopyranose.

(11) by GC–MS analysis. No peak was found ascribable to 6-(2-mercaptoethylamino)-6-deoxyglucose, indicating that the amino group in 2-aminoethanethiol did not react with halodeoxycellulose under the conditions used.

Figure 6 shows the GC chromatogram for the hydrolysate of bromodeoxycellulose treated with 3-mercaptopropanoic acid. Peaks h and i were TFA derivatives of mono- and dibromo derivatives of cellobiose often found for the hydrolysates of bromodeoxycellulose (Aoki *et al.*, 1994). Peaks f and g were tentatively assigned to those of trifluoroacetate of lactone of 6-(2-carboxyethylthio)-6-deoxyglucose (12) (Fig. 7). The assignment was based on the Br-free molecular ion of *m/z* 538 (Table 4). Formation of lactone is not unrealistic. Niemelä and Sjöström (1988, 1989) reported the formation of lactones from carboxymethylcellulose by acid hydrolysis.

Table 3 shows mass fragmentation patterns of (6), (7), (9) and (11) as their TFA derivatives. All 6-thioglucose derivatives clearly gave their molecular ions. Compound (7) gave its molecular ions very abundantly due to its aromatic nature. Concerning the mass fragmentation patterns, 6-thioglucose derivatives gave only A_1–A_3 and E_3 fragment ions out of the typical fragment ions of glucose derivatives (Kochetokov & Chizhov, 1966). Their thioether structures had more influence on the course of fragmentation of the thio derivatives. Because of the lack of the usual fragment ions of glucose derivatives, the ring forms of these compounds could not be determined by the interpretation of mass fragmentation patterns.

Table 3. Mass fragmentation pattern(s) of TFA derivatives of hydrolysates of the sample treated with thiols

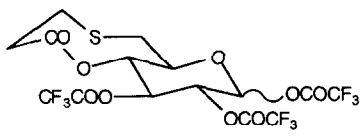
Peak/Fig. No. assignment	Peak b/Fig. 2 (6)		Peak c/Fig. 2 (6)		Peak e/Fig. 3 (7)		Peak e/Fig. 4 (9)		Peak d/Fig. 5 (11)	
	m/z	r.a.	*m/z*	r.a.	*m/z*	r.a.	*m/z*	r.a.	*m/z*	r.a.
M^+	594	1·8	594	3·9	656	50·2	720	0·1	719	0·3
M-CF_3COO	481	6·8	481	2·2	543	4·5	607	8·4	606	21·6
M-CF_3COO-CF_3COOH	367	1·6	367	0·5	429	0·7	493	0·9	492	3·5
M-CF_3COO-2CF_3COOH	253	4·3	253	3·7	315	0·9	379	4·8	378	1·5
M-SR-CF_3COO-CF_3COOH	433	13·6	433	1·5	433	0	433	0·2	433	0·1
M-SR-CF_3COO-2CF_3COOH	319	2·6	319	5·7	319	1·9	319	12·1	319	3·7
M-CH_2SR-2CF_3COOH	305	3·0	305	0	305	0·1	305	0·7	305	1·1
CH_2SRCH	61	100	61	100	123	100	187	30·1	186	6·9
CF_3COOCH_2SR	187	4·2	187	1·7	249	1·1	313	0·7	312	0
$CHCH_2SR$	73	2·8	73	2·7	135	5·9	199	28·6	198	0·7
SR	47	[b]	47	[b]	109	14·5	173	1·3	172	8·3
R[a]	15	[b]	15	[b]	77	1·8	141	100	140	57·2
CF_3	69	38·0	69	33·2	69	12·0	69	52·9	69	42·9
CH_2CH_2S	60	0	60	0·5	60	0	60	98·6	60	100

[a]R is CH_3, C_6H_5, $CH_2CH_2OCOCF_3$ and $CH_2CH_2NHCOCF_3$ for (6), (7), (9) and (11), respectively.
[b]Intensities of ions of mass numbers lower than 50 were not measured.
m/z, mass number; r.a., relative abundance (%).

Table 4. Important mass fragment ions of TFA derivatives of 3-chloro-3-deoxyalloses

Peak		Tentative assignment[a]	Mass fragmentation pattern *m/z* (r.a., %) [assignment]
Fig. 3	peak f	(8)	578[b] (47·2) [M], 465[b] (1·6) [M-CF_3COO], 351[b] (0·4) [M-CF_3COO-CF_3COOH], 319 (0·5) [M-SPh-HCl-CF_3COOH], 241[b] (1·10) [M-SPh-2CF_3COOH], 227[b] (2·2) [M-CH_2-S-Ph-2CF_3COOH], 123 (100) [CH_2SPh], 109 (20·3) [SPh], 69 (18·0) [CF_3]
	peak g	(8)	578[b] (21·7) [M], 465[b] (2·3) [M-CF_3COO], 319 (2·0) [M-SPh-HCl-CF_3COOH], 241[b] (16·3) [M-SPh-2CF_3COOH], 123 {100} [CH_2SPh], 109 (20·3) [SPh], 69 (18·0) [CF_3]
	peak i	(8)	578[b] (18·5) [M], 465[b] (3·0) [M-CF_3COO], 319 (1·3) [M-SPh-HCl-CF_3COOH], 241[b] (12·6) [M-SPh-2CF_3COOH], 123 [100] [CH_2SPh], 109 (16·8) [SPh], 69 (21·1) [CF_3]
Fig. 4	peak g	(10)	642[b] (0·3) [M], 607 (0·2) [M-Cl], 529[b] (21·6) [M-CF_3COO], 493 (0·9) [M-Cl-CF_3COOH], 415[b] (2·0) [M-CF_3COO-CF_3COOH], 379 (1·9) [M-Cl-2CF_3COOH], 301[b] (1·3) [M-CF_3COO-2CF_3COOH], 199 (3·6) [CH_2=CS-$CH_2CH_2OCOCF_3$], 173 (2·3) [$SCH_2CH_2OCOCF_3$], 141(100) [$CH_2CH_2OCOCF_3$], 69 (53·7) [CF_3], 60 (87·2) [CH_2CH_2S]
	peak h	(10)	642[b] (0·3) [M], 607 (0·4) [M-Cl], 529[b] (10·5) [M-CF_3COO], 493 (1·2) [M-Cl-CF_3COOH], 415[b] (6·2) [M-CF_3COO-CF_3COOH], 379 (2·7) [M-Cl-2CF_3COOH], 301[b] (0·8) [M-CF_3COO-2CF_3COOH], 199 (100) [CH_2=C-S-$CH_2CH_2OCOCF_3$], 187 (26·8) [$CH_2SCH_2CH_2OCOCF_3$], 173 (3·5) [$SCH_2CH_2OCOCF_3$], 141 (62·8) [$CH_2CH_2OCOCF_3$], 69 (63·7) [CF_3], 60 (37·3) [CH_2CH_2S]
	peak i	(10)	642[b] (trace) [M], 607 (0·9) [M-Cl], 529[b] (5·9) [M-CF_3COO], 493 (1·6) [M-Cl-CF_3COOH], 415[b] (1·4) [M-CF_3COO-CF_3COOH], 379 (18·9) [M-Cl-2CF_3COOH], 301[b] (2·4) (M-CF_3COO-2CF_3COOH], 199 (4·0) [CH_2=C-S-$CH_2CH_2OCOCF_3$], 187 (100) [$CH_2SCH_2CH_2OCOCF_3$], 173 (1·1) [$SCH_2CH_2OCOCF_3$], 141 (89·2) [$CH_2CH_2OCOCF_3$], 69 (52·7) [CF_3], 60 (8·3) [CH_2CH_2S]
Fig. 6	peak g	(12)	538 (25·1) [M], 510 (0·5) [M-CO], 425 (14·0) [M-CF_3COO], 397 (9·3) [M-CO-CF_3COO], 368 (3·4) [M-CO-HCHO-CF_3COO], 336 (31·4) [M-CO-HCHO-CF_3COO-S], 222 (25·2) [M-CO-HCHO-S-CF_3COO-CF_3COOH], 97 (22·7) [CF_3CO], 88 (78·6) [SCH_2CH_2CO], 69 (82·5) [CF_3], 60 (32·1) [CH_2CH_2S], 55 (100) [CH_2=CHCHO]

[a]The ring structure could not be clarified from mass spectral data.
[b]Accompanying (*A* + 2) ions, due to the presence of a chlorine atom, were observed.



Trifluoroacetates of **12**

Fig. 7. Trifluoroacetates of (12).

REFERENCES

Aoki, N., Suzuki, S., Furuhata, K. & Sakamoto, M. (1994). *Sen'i Gakkaishi*, **50,** 515–9.

Furuhata, K., Chang, H.-S., Aoki, N. & Sakamoto, M. (1992*a*). *Carbohydr. Res.*, **230,** 151–64.

Furuhata, K., Chang, H.-S., Koganei, K. & Sakamoto, M. (1992*b*). *Sen'i Gakkaishi*, **48,** 602–9.

Furuhata, K., Koganei, K., Chang, H.-S., Aoki, N. & Sakamoto, M. (1992*c*). *Carbohydr. Res.*, **230,** 165–77.

Kinoshita, M. & Hozumi, K. (1965). *Bunseki Kagaku*, **14,** 352–4.

Kochetokov, N.K. & Chizhov, O.S. (1966). *Adv. Carbohydr. Chem. Biochem.*, **29,** 41–106.

Niemelä, K. & Sjöström, E. (1988). *Carbohydr. Res.*, **180,** 43–52.

Niemelä, K. & Sjöström, E. (1989). *Polym. Commun.*, **30,** 254–6.

Rowland, S.P., Cirino, V.O. & Bullock, A.L. (1966). *Can. J. Chem.*, **44,** 1051–8.

Vigo, T.L. & Welch, C.M. (1970). *Text. Res. J.*, **40,** 109–15.