Optical Resolution on Regioselectively Carbamoylated Cellulose and Amylose with 3,5-Dimethylphenyl and 3,5-Dichlorophenyl Isocyanates

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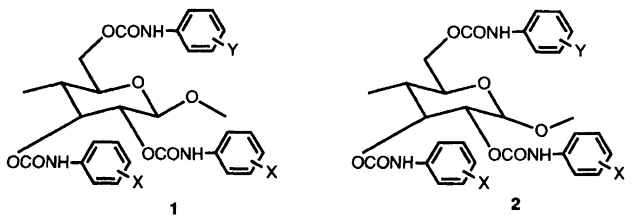
The optical resolving ability of two types of regioselectively carbamoylated cellulose and amylose with 3,5-dimethylphenyl and 3,5-dichlorophenyl isocyanates was evaluated. One had 3,5-dimethylphenylcarbamate groups at the 2 and 3 positions and a 3,5-dichlorophenylcarbamate group at the 6 position; the other had 3,5-dichlorophenylcarbamate groups at the 2 and 3 positions and a 3,5-dimethylphenylcarbamate group at the 6 position. In cellulose derivatives, the side chains at the 2,3, and 6 positions seem to interact complicatedly with racemates. On the other hand, in the amylose derivatives, the side chains at the 2 and 3 positions may mainly influence the chiral recognition ability. The optical resolving abilities of the cellulose and amylose derivatives having irregularly either 3,5-dimethylphenyl- or 3,5-dichlorophenylcarbamate groups at the 2,3, and 6 positions were also examined.

We previously reported that phenylcarbamate derivatives of cellulose[1,2] and amylose[3] show a high optical resolving ability as chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC). Among the derivatives, tris(3,5-dimethylphenylcarbamate) (**1a**, **2a**) and tris(3,5-dichlorophenylcarbamate) (**1b**, **2b**) show a high optical resolving power for many racemates (Chart 1).[2—4] However, no precise information has been obtained concerning the mechanism of chiral recognition on these derivatives. Therefore, we studied the optical resolving ability of two types of regioselectively carbamoylated cellulose and amylose with 3,5-dimethylphenyl or 3,5-dichlorophenyl isocyanates in order to understand the mechanism of the optical resolution on these polysaccharide derivatives, and to develop a new chiral stationary phase with a high optical resolving power. We thus prepared two types of regioselectively carbamoylated cellulose and amylose with 3,5-dimethylphenyl or 3,5-dichlorophenyl isocyanates and evaluated their optical resolving ability. One had 3,5-dimethylphenylcarbamate groups at the 2 and 3 positions and a 3,5-dichlorophenylcarbamate group at the 6 position (**1c**, **2c**); the other had 3,5-dichlorophenylcarbamate groups at the 2 and 3 positions and a 3,5-dimethylphenylcarbamate group at the 6 position (**1d**, **2d**). The optical resolving ability of the derivatives of cellulose (**1e**, **f**) and amylose (**2e**, **f**), which had randomly 3,5-dimethylphenyl- and 3,5-dichlorophenylcarbamate groups at the 2,3, and 6 positions, was also appreciated.



a: X, Y = 3,5-Me_2 b: X, Y = 3,5-Cl_2
c: X = 3,5-Me_2, Y = 3,5-Cl_2 d: X = 3,5-Cl_2, Y = 3,5-Me_2
e: X, Y=3,5-Me_2, 3,5-Cl_2 (2:1) f: X, Y=3,5-Me_2, 3,5-Cl_2 (1:2)

Chart 1.

Experimental

A cellulose derivative (**1c**) having 3,5-dimethylphenylcarbamate groups at the 2 and 3 positions and a 3,5-dichlorophenylcarbamate group at the 6 position was synthesized as shown in Scheme 1. First, cellulose was allowed to react with triphenylmethyl chloride, which can react with only the primary hydroxyl group at the 6 position to form trityl ether,[5] in pyridine at 80 °C about 24 h. Then, an excess of 3,5-dimethylphenyl isocyanate was added to react with the hydroxyl groups at the 2 and 3 positions. The thus-obtained 2,3-bis(3,5-dimethylphenylcarbamoyl)-6-*O*-trityl cellulose was suspended in methanol containing a small amount of hydrochloric acid so as to remove the triphenylmethyl group at room temperature. The obtained cellulose 2,3-bis-(3,5-dimethylphenylcarbamate) was allowed to react with 3,5-dichlorophenyl isocyanate to prepare cellulose 2,3-bis-(3,5-dimethylphenylcarbamate)-6-(3,5-dichlorophenylcarbamate) (**1c**). Cellulose 2,3-bis(3,5-dichlorophenylcarbamate)-6-(3,5-dimethylphenylcarbamate) (**1d**) was prepared in a similar way.

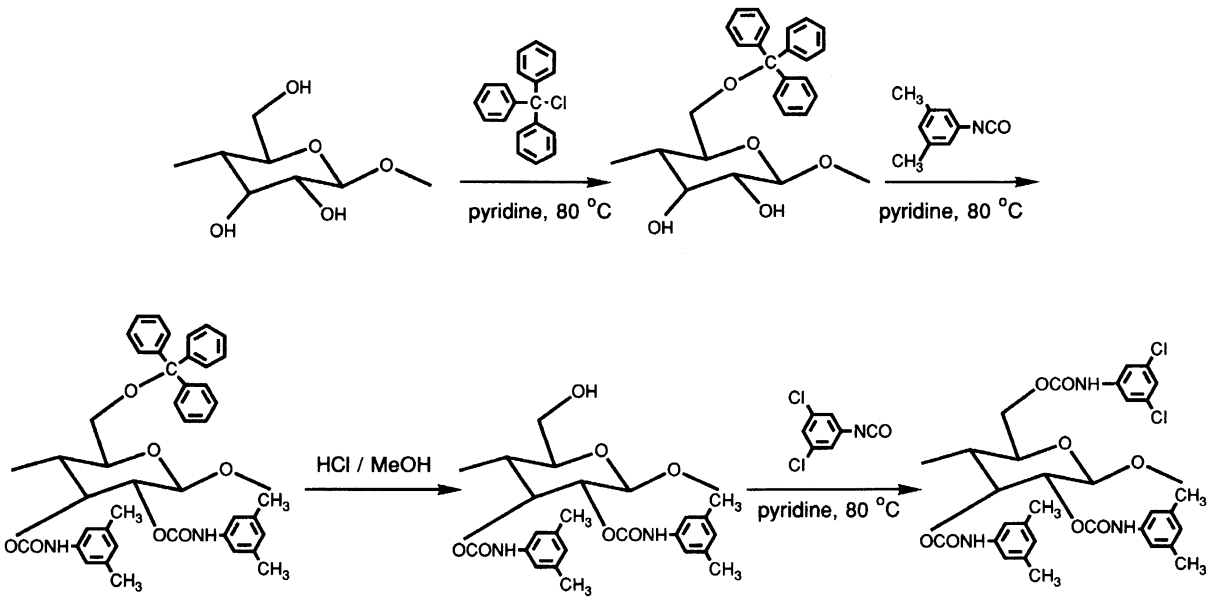
Cellulose derivatives (**1e**, **f**) bearing irregularly either a 3,5-dimethylphenyl- or 3,5-dichlorophenylcarbamate moiety at the 2,3, and 6 positions were synthesized by a reaction of cellulose with 2 to 1 or 1 to 2 mixtures of 3,5-dimethylphenyl and 3,5-dichlorophenyl isocyantes.

Amylose derivatives (**2c**—**f**) were prepared by analogous methods, as described for the above-mentioned cellulose derivatives (**1c**—**f**).

These products were identified by ^{1}H NMR spectroscopy (Figs. 1 and 2) and elemental analysis (Table 1).

The packing materials were prepared as previously reported.[6] Each packing material was packed in a stainless-steel tube (25 cm×0.46 (i. d.) cm) by a slurry method. The theoretical plate numbers of the columns for benzene were from 3200 to 4300.

Chromatographic resolution was accomplished on a JASCO BIP-I chromatograph equipped with a JASCO 875-UV (254 nm) and a JASCO DIP-181C polarimetric detec-



Scheme 1.

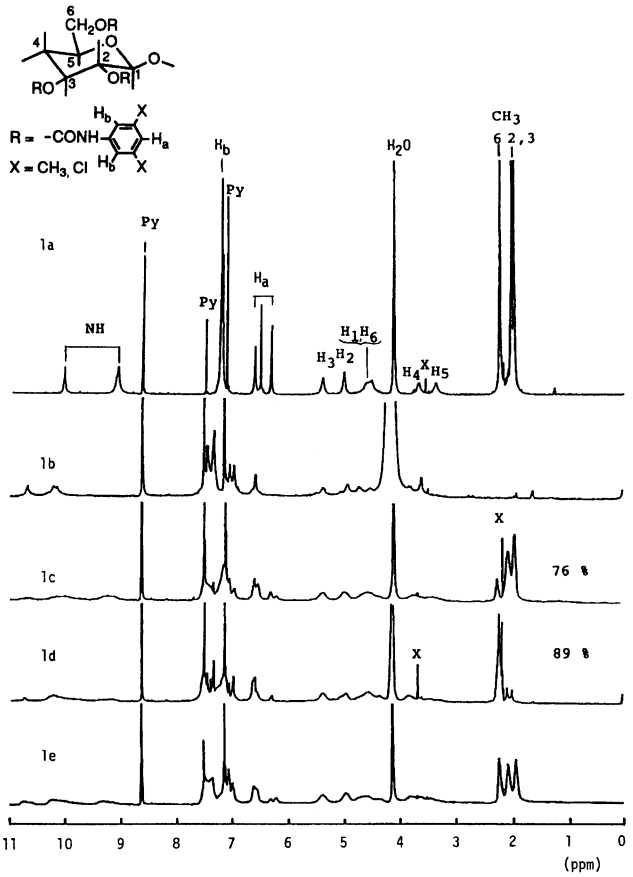


Fig. 1. ^{1}H NMR spectra of cellulose derivatives (**1a**—**e**). (Pyridine-d_5, 80 °C, 500 MHz).

tor (Hg, without filters). Separation was carried out with a hexane-2-propanol mixture (90 : 10 or 95 : 5) at a flow rate of 0.5 ml min^{-1}. The dead time (t_0) was estimated with 1,3, 5-tri-*t*-butylbenzene.[7] The ^{1}H NMR spectra were measured with a Varian VXR500 (500 MHz) spectrometer using TMS

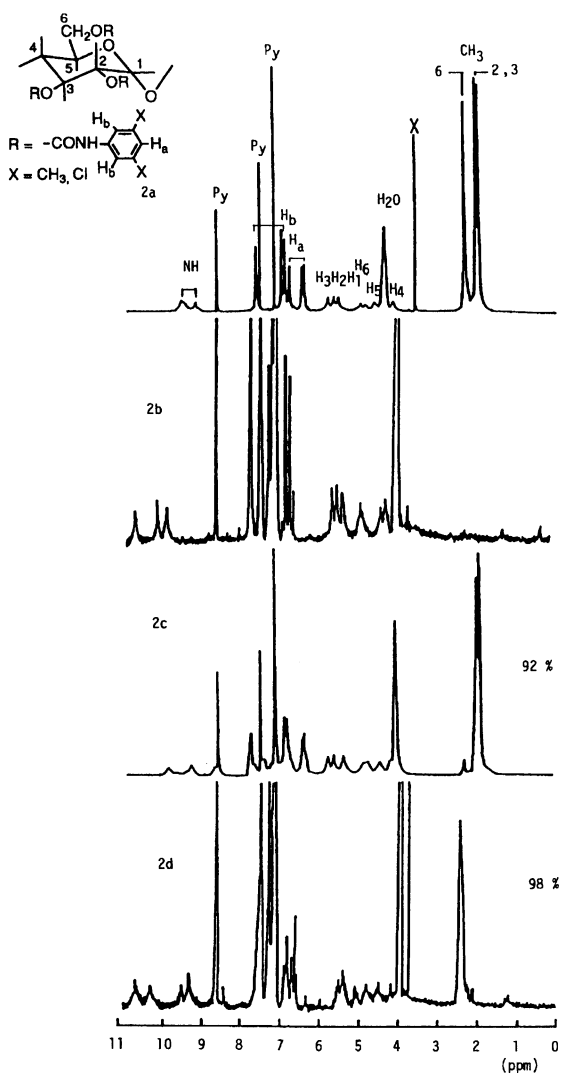


Fig. 2. ^{1}H NMR spectra of amylose derivatives (**2a**—**d**). (Pyridine-d_5, 80 °C, 500 MHz).

Table 1. Elemental Analyses and Contents of 3,5-Dimethylphenyl- (Me) and 3,5-Dichlorophenylcarbamate (Cl) Residues Calculated from Cl % of **1c**—**f** and **2c**—**f**[a)]

		C%	H%	N%	Cl%
1c	Found	59.65	5.03	6.66	9.45
	Calcd	(58.89	5.00	6.58	9.45)
		(Me : Cl=2.15 : 0.85)[b)]			
1d	Found	50.66	3.31	6.13	21.29
	Calcd	(50.41	3.58	6.11	21.29)
		(Me : Cl=0.94 : 2.06)[b)]			
1e	Found	58.26	5.03	6.65	10.76
	Calcd	(57.99	4.85	6.53	10.76)
		(Me : Cl=2.03 : 0.97)[b)]			
1f	Found	51.02	3.84	6.21	19.88
	Calcd	(51.40	3.75	6.17	19.88)
		(Me : Cl=1.09 : 1.91)[b)]			
2c	Found	57.33	4.77	6.33	10.39
	Calcd	(58.21	4.89	6.55	10.39)
		(Me : Cl=2.06 : 0.94)[b)]			
2d	Found	51.21	4.12	6.25	20.69
	Calcd	(50.86	3.66	6.14	20.69)
		(Me : Cl=1.01 : 1.99)[b)]			
2e	Found	58.34	4.93	6.06	10.02
	Calcd	(58.51	4.94	6.56	10.02)
		(Me : Cl=2.09 : 0.91)[b)]			
2f	Found	50.19	3.97	6.07	20.48
	Calcd	(51.00	3.68	6.14	20.48)
		(Me : Cl=1.03 : 1.97)[b)]			

a) Calculated values for contents of Me and Cl obtained from Cl % are shown in parentheses. b) Contents of 3,5-dimethylphenyl- (Me) and 3,5-dichlorophenylcarbamate (Cl) residues calculated from Cl % of tris(carbamate) derivatives.

as an internal standard. The IR spectra were measured with a JASCO IR 810 spectrophotometer as KBr pellets.

Results and Discussion

Figures 1 and 2 show the ^{1}H NMR spectra of cellulose derivatives (**1a**—**e**) and amylose derivatives (**2a**—**d**), respectively. All peaks of **1a** and **2a** were assigned on the basis of ^{1}H–^{1}H COSY spectra of **1a** and **2a**.[8)] In the spectrum of **1a**, three peaks, which were assigned to the two methyl groups on the phenyl groups at the 2,3, and 6 positions, were observed at about 2 ppm. In **1b**, such peaks were not present. In the spectrum of **1c**, the peak due to the methyl group at the 6 position at 2.2 ppm was small compared with the peaks due to the methyl groups of the 2 and 3 positions at 1.8 and 2.0 ppm, whereas in the spectrum of **1d**, the peaks at 1.8 and 2.0 ppm were smaller than that at 2.2 ppm. These results indicate that three hydroxyl groups were regioselectively converted into 3,5-dimethylphenyl- or 3,5-dichlorophenylcarbamate groups. From these results of the ^{1}H NMR spectra and elemental analysis, the regioselectivity at the 6 position for **1c** and **1d** was estimated to be 76 and 89%, respectively. Thus, 76% of the hydroxyl group at the 6 position of **1c** was converted into the 3,5-dichlorophenylcarbamate moiety and 24% was 3,5-dimethylphenylcarbamate moiety, and 95% of the hydroxyl groups at the 2 and 3 positions were converted into the 3,5-dimethylphenylcarbamate moiety, and 5% were the 3,5-dichlorophenylcarbamate moiety. In the case of **1e**, the intensities of these peaks were almost the same. This indicates that three hydroxyl groups were converted non-regioselectively into the 3,5-dimethylphenyl- or 3,5-dichlorophenylcarbamate moiety. Similar results were obtained in amylose derivatives (Fig. 2), and the regioselectivity at the 6 position for **2c** and **2d** was 92 and 98%, respectively.

Figure 3 shows a chromatogram of the resolution of racemate **3** on a column packed with cellulose derivative **1c**. The enantiomers eluted at retention times of t_1 and t_2 and were completely separated. The capacity factors (k'_1 and k'_2), which were evaluated as $(t_1-t_0)/t_0$ and $(t_2-t_0)/t_0$, were 0.44 and 0.60, respectively. The separation factor ($\alpha=k'_2/k'_1$) and the resolution factor ($R_s=2(t_2-t_1)/(W_1+W_2)$) were determined to be 1.37 and 1.82, respectively.

Table 2 shows the results of the optical resolution of racemates **3**—**12** on cellulose derivatives **1c**—**f** (Chart 2). The results on tris(3,5-dimethylphenylcarbamate) (**1a**) and tris(3,5-dichlorophenylcarbamate) (**1b**) of cellulose are also shown for a comparison. The optical resolving abilities of these cellulose derivatives depended greatly on the racemates. For example, in the resolution of **9**, the (−) isomer eluted first on **1a**, but the (+) isomer eluted first on **1b**. This result indicates that the mechanism of chiral recognition of **1a** for **9** is different from that of **1b**. As for the resolution

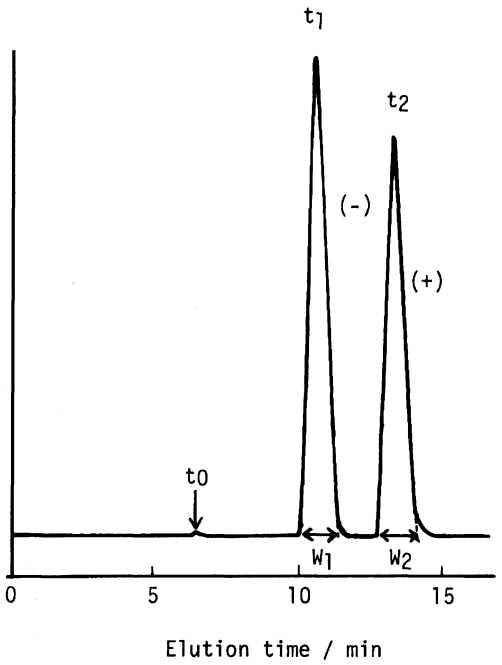


Fig. 3. Optical resolution of **3** on **1c**. (Hexane–2-propanol (90 : 10), 0.5 ml min^{-1}, 25 °C).

Table 2. Optical Resolution of Racemates (**3**—**12**) on Cellulose Tris(phenylcarbamate)s (**1a**—**f**)[a]

	1a		**1b**[b]		**1c**			**1d**[b]			**1e**			**1f**		
	k_1'[c]	α	k_1'[c]	α	k_1'[c]	α	R_s	k_1'[c]	α	R_s	k_1'[c]	α	R_s	k_1'[c]	α	R_s
3	2.13(−)	2.59	0.28(−)	1.38	0.44(−)	1.37	1.68	0.77(−)	1.55	1.49	0.45(−)	1.72	2.01	0.37(−)	1.50	1.56
4	0.97(−)	1.32	0.87(+)	1.65	0.52(+)	1.39	1.54	0.82(+)	1.22	1.32	0.46(+)	1.32	1.22	0.53(+)	1.84	2.31
5	2.43(+)	1.58	3.08(−)	1.21	2.64(−)	1.15	0.67	2.84(+)	1.13	0.82	1.37(+)	1.19	1.02	2.08(−)	1.07	
6	1.37(+)	1.34	0.40(+)	1.29	0.43(+)	1.14	0.78	0.87(−)	ca. 1		0.48(+)	ca. 1		0.47(+)	ca. 1	
7	1.17(+)	1.15	2.65(−)	1.26	0.97(−)	1.28	1.15	1.36(−)	1.20	1.20	0.69(−)	1.22	1.32	1.02(−)	1.20	1.18
8	1.47(−)	1.41	1.55(−)	1.20	0.77(−)	1.15		1.21(−)	1.12		0.63(−)	1.22	1.04	0.37(−)	1.50	1.67
9	0.47(−)	1.68	0.56(+)	1.84	0.35(+)	1.80	2.10	0.50(+)	1.33	1.24	0.37(−)	ca. 1		0.36(+)	2.03	4.34
10	0.42(+)	ca. 1	0.76(+)	1.82	0.47(+)	1.50	1.86	1.26(+)	1.16	0.73	0.45(−)	1.72	1.98	0.36(+)	1.69	1.56
11	2.36(−)	1.83	1.62(+)	1.11	1.08(−)	1.30	1.54	2.26(−)	1.28	1.37	1.01(−)	1.82	2.13	1.48(−)	1.36	1.44
12	0.83(+)	3.17	0.59(+)	1.41	0.68(+)	1.20	1.20	0.89(+)	ca. 1		0.49(+)	1.17	0.64	0.66(+)	ca. 1	

a) Eluent: hexane–2-propanol (90 : 10), 0.5 ml min^{-1}, 25 °C. b) Hexane–2-propanol (95 : 5). c) The sign in parentheses shows optical rotation of the first-eluted isomer.

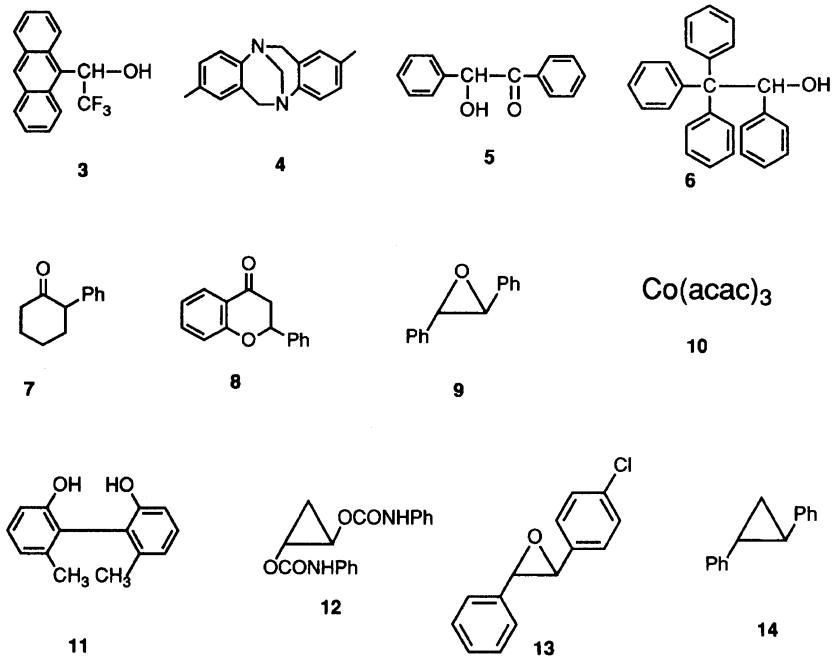


Chart 2.

of **9**, **1c** and **1d** showed a similar enantioselectivity to that of **1b**, eluting the (+) isomer first. A similar chiral discrimination seems to proceed on **1b**,**1c**, and **1d** for **9**. These results may be explained in the following way. The most important adsorbing site of the cellulose derivatives for chiral recognition may be the carbamate residue (Fig. 4).[2] The polarity of the residue is influenced by the substituents on the phenyl groups. If an electron-donating substituent, such as methyl group, is introduced on the phenyl group, the electron density of the carbonyl group is enhanced, and if an electron-withdrawing group such as the chloro group is introduced, the acidity of the NH group becomes higher. These inductive effects can be expected from the difference in the chemical shifts of the NH-protons between **1a** and **1b**, as shown in Fig. 1. The NH-protons resonances of **1b** shift down field compared with those of **1a**. These chemical shifts of the NH-protons are little influenced

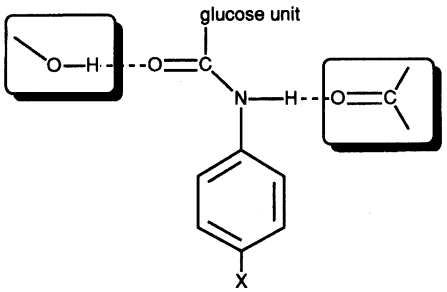


Fig. 4. Schematic interaction of the racemic compounds with the residue of CSP.

by the presence of a small amount of water. For example, the chemical shifts of the NH-protons of **1a** were scarcely changed by the addition of about a 10-times molar quantity of D_2O to one glucose residue of **1a**. The racemates probably interact with the carbamate

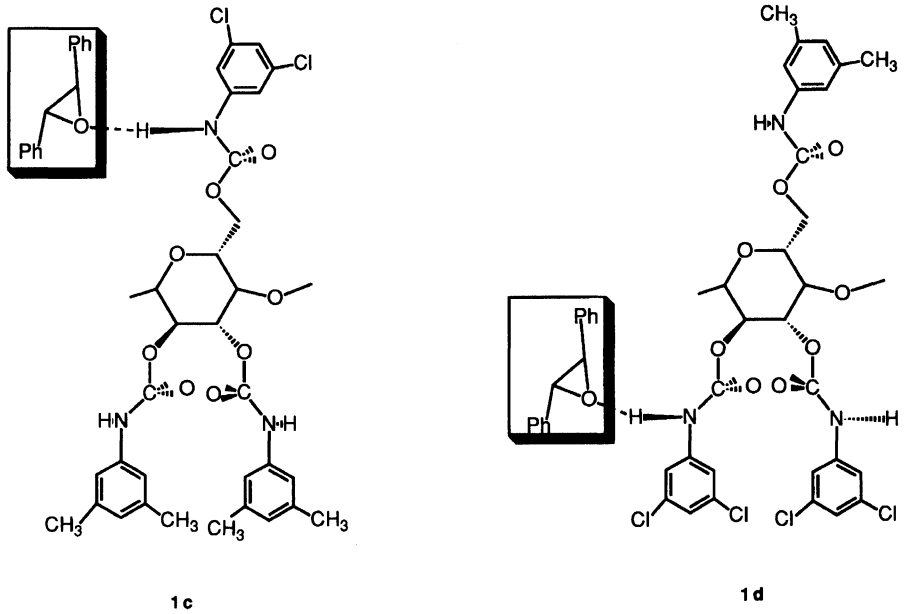


Fig. 5. Schematic interaction of **9** with **1c** and **1d**.

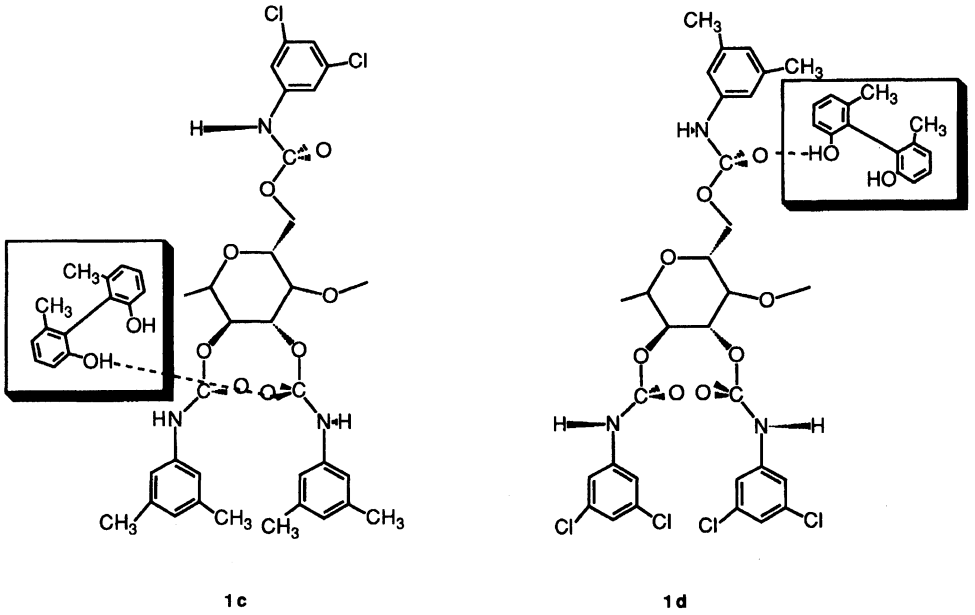


Fig. 6. Schematic interactions of **11** with **1c** and **1d**.

residues through the hydrogen bond, as shown in Fig. 4. The ether oxygen of **9** appears to be the most important site for an interaction with these CSPs. The ether oxygen can interact with the NH-proton. On the basis of these speculations, it is likely that **9** may interact more strongly with the NH group of the 3,5-dichlorophenylcarbamate residue than that of the 3,5-dimethylphenylcarbamate residue. Thus, as shown in Fig. 5, **9** may interact with 3,5-dichlorophenylcarbamate at the 6 position on **1c** and at the 2 or 3 position on **1d**. It is interesting that **1f** shows a high optical resolving ability for **9**. This suggests that if two hydroxyl groups at the 2 and 3 positions are converted into different kinds of carbamate residues, a higher chiral recognition might be attained.

In the resolution of **11**, the (−) isomer eluted first on **1a**, **1c**, and **1d**, while the (+) isomer eluted first on **1b**. This indicates that for **11**, the mechanism of chiral separation on **1a**, **1c**, and **1d** may be different from that on **1b**. The most important site of **11** for the interaction with the CSPs seems to be the hydroxyl group. Therefore, **11** may interact mainly with the carbonyl group of the 3,5-dimethylphenylcarbamate residue at the 2 or 3 position on **1c** and at the 6 position on **1d** (Fig. 6). However, such an interaction on **1b** is impossible, and the oxygen of the hydroxyl groups of **11** may mainly in-

Table 3. Optical Resolution of Racemates (**13**, **14**, and **9**) on Cellulose Tris(phenylcarbamate)s (**1a**—**d**)[a]

	1a			**1b**[b]			**1c**			**1d**[b]		
	k_1'[c]	α	R_s	k_1'[c]	α	R_s	k_1'[c]	α	R_s	k_1'[c]	α	R_s
13	1.66(1S, 2S)	1.42	1.90	0.33(1R, 2R)	1.23	1.80	0.25(1R, 2R)	1.60	1.22	0.37(1R, 2R)	1.17	
14	0.53(1R, 2R)	1.38	1.55	0.17(1R, 2R)	ca. 1		0.22(1R, 2R)	ca. 1		0.21(1R, 2R)	ca. 1	
9	0.47(1S, 2S)	1.68	2.80	0.56(1R, 2R)	1.84	3.62	0.35(1R, 2R)	1.80	2.10	0.50(1R, 2R)	1.33	1.24

a) Eluent: hexane–2-propanol (90 : 10), 0.5 ml min^{-1}, 25 °C. b) Hexane–2-propanol (95 : 5). c) Absolute configuration of the first-eluted isomers are shown in parentheses.

Table 4. Optical Resolution of Racemates (**3**—**12**) on Amylose Tris(phenylcarbamate)s (**2a**—**f**)[a]

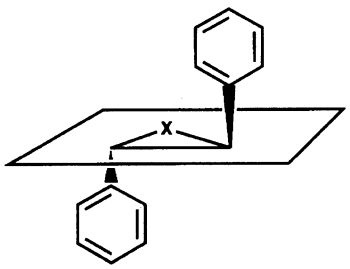
	2a		**2b**		**2c**			**2d**			**2e**			**2f**		
	k_1'[b]	α	k_1'[b]	α	k_1'[b]	α	R_s	k_1'[b]	α	R_s	k_1'[b]	α	R_s	k_1'[b]	α	R_s
3	1.30(+)	1.15	0.37	1.00	0.73(+)	1.16	0.80	0.27(+)	ca. 1		2.35(+)	ca. 1		2.43(+)	ca. 1	
4	0.53(+)	1.58	0.84(+)	1.34	0.93(+)	1.42	1.90	0.53(+)	1.43	1.80	0.57(+)	1.25	1.22	1.23	1.00	
5	3.14(−)	1.21	6.08(+)	ca. 1	5.83(−)	1.11	0.89	1.86(+)	1.70	2.62	2.11(−)	1.15		2.76(−)	ca. 1	
6	2.65(+)	1.98	0.88(+)	2.25	1.16(+)	1.73	2.00	0.44(+)	2.30	2.29	3.67(+)	ca. 1		2.08	1.00	
7	0.61(−)	ca. 1	0.63(+)	ca. 1	0.85(−)	ca. 1		1.53(+)	ca. 1		1.22	1.00		0.80(−)	ca. 1	
8	0.93(+)	1.12	1.62(+)	1.10	1.29(+)	1.14	0.59	1.00(+)	1.07		1.32(+)	1.04		1.33	1.00	
9	0.42(+)	3.04	0.50(+)	1.32	0.71(+)	1.45	2.07	0.40(+)	ca. 1		0.36(+)	ca. 1		0.40(+)	ca. 1	
10	0.25(−)	ca. 1	0.63(+)	ca. 1	0.73(+)	ca. 1		0.47(−)	ca. 1		0.93(+)	1.08		2.23	1.00	
11	2.46(−)	2.11	1.10(+)	ca. 1	3.57(−)	1.51	2.39	0.51(+)	1.18	1.04	2.14(−)	1.10		2.58(−)	ca. 1	
12	3.25(+)	2.01	0.59(−)	1.10	3.40(+)	1.45	2.27	0.40(−)	ca. 1		1.37(−)	1.11		1.30(−)	ca. 1	

a) Eluent: hexane–2-propanol (90 : 10), 0.5 ml min^{-1}, 25 °C. b) The sign in parenthese shows optical rotation of the first-eluted isomer.

teract with the NH of the 3,5-dichlorophenylcarbamate residue.

In the resolution of **5**, **1a**, and **1d** showed the same enantioselectivity, and **1b** and **1c** also showed the same enantioselectivity, which is opposite to that of **1a** and **1d**. These results suggest that the carbamate residue at the 6 position of the CSPs may play an important role for the chiral recognition of **5**. In the chiral separation of **7** and **12**, no reversal of the elution order of the enentiomers was observed. However, **7** seems to be mainly discriminated by the 3,5-dichlorophenylcarbamate group, since **7** was resolved on **1c** and **1d** with almost the same α value as that on **1b**. Probably, the carbonyl oxygen of **7** approaches to the NH of 3,5-dichlorophenylcarbamate group. On the other hand, the optical resolving abilities of **1c**—**f** for **12** became quite low compared with that of **1a**. This suggests that **12** is likely to interact simultaneously with multiple 3,5-dimethylphenylcarbamate residues, for instance, those at the 2,3 positions and at the 6 position of neighboring glucose units.

The results of the optical resolution of **13** and **14** on **1a**—**d** are summarized in Table 3. The data on a similar compound **9** are also shown for a comparison. The resolution of the three racemates on **1a** proceeded in a similar way in respect to the stereochemistry, as shown in Fig. 7. However, on **1b**, **1c**, and **1d**, **14** was not resolved. These results imply that the chiral recognition mechanism on **1a** may be different from that on the other three CSPs; on **1a**, a π–π interaction between the phenyl groups of the solutes and the CSP may be the



9: X= O, (1S, 2S)-(-)
14: X= CH_2, (1R, 2R)-(+)

Fig. 7. Conformation of the enantiomers of **9** and **14** adsorbed more strongly to **1a**.

controlling force for chiral discrimination and on **1b**, **1c**, and **1d**, hydrogen bonding between the ether oxygen of the solutes and the NH group of CSPs may be the most important interaction. Such an interaction is impossible for **14**.

The results of the optical resolution of **3**—**12** on amylose derivatives (**2a**—**f**) are listed in Table 4. In the amylose derivatives, the enantioselectivity of **2a** was similar to that of **2c**, and **2b** showed an analogous chiral discrimination to **2d**. For example, **3** was resolved on **2c** with almost the same α value as that on **2a**, though neither **2b** nor **2d** resolved **3**. For **6**, **2c** showed almost the same chiral recognition ability as that of **2a**. These results suggest that the mechanism of chiral separation on **2c** may be similar to that on **2a**, and that the mechanism on **2d** may be analogous to that on **2b**. For most racemates, except for **4**—**6**, **2c** showed a higher optical

resolving ability than did **2d**, and except for **6**, **2a** was superior to **2b**. The chiral recognition abilities of **2e** and **2f** were also lower than that of **2c**. These results indicate that the side groups at the 2 and 3 positions of the amylose derivatives are more important of the optical resolution than that at the 6 position.

The difference observed between the cellulose and amylose derivatives can be explained as follows. Figures 8 and 9 show the possible structures of the phenylcarbamates of cellulose[9] and amylose,[10] respectively, reported by P. Zugenmaier et al. on the basis of X-ray analysis. The cellulose derivative possesses a conformation of a left-handed threefold (3/2) helix. Therefore, recemates can interact with the carbamate moieties of the side chains complicatedly, since the side chains at the 2,3 positions and the 6 position of the neighboring glucose units are located close to each other. Therefore, racemic compounds can interact with these carbamate residues simultaneously. On the other hand, the conformation of the amylose derivative is a left-handed fourfold (4/1) helix. The racemates cannot interact simultaneously with the carbamate residues at the 2 or 3 position and the 6 position of the neighboring glucose units, since these are remote from each other. Thus, in the cellulose derivatives, the carbamate residue at the 6 position may be for chiral recognition as important as those at the 2 and 3 positions. However, in the amylose derivatives, the carbamate residues at the 2 and 3 positions seem to be more important than that isolated at the 6 position.

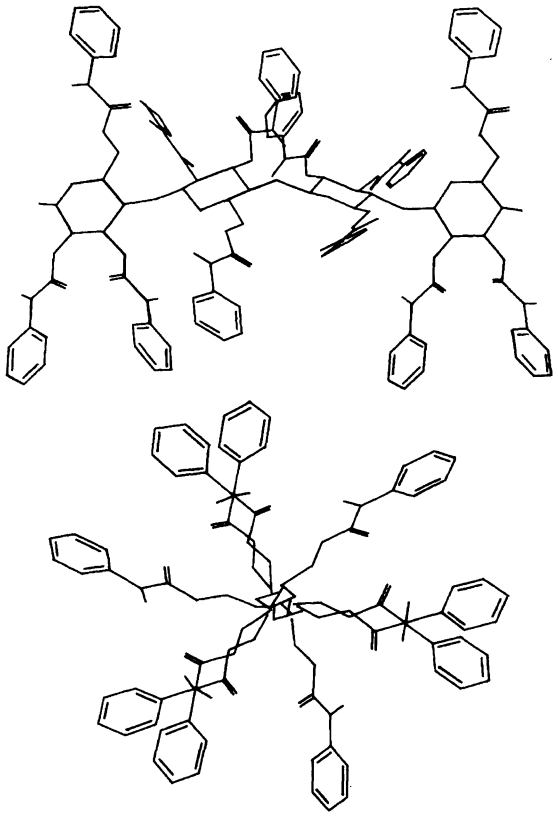


Fig. 8. Structure of cellulose tris(phenylcarbamate). Top: along the chain axis; bottom: perpendicular to the chain axis.[9]

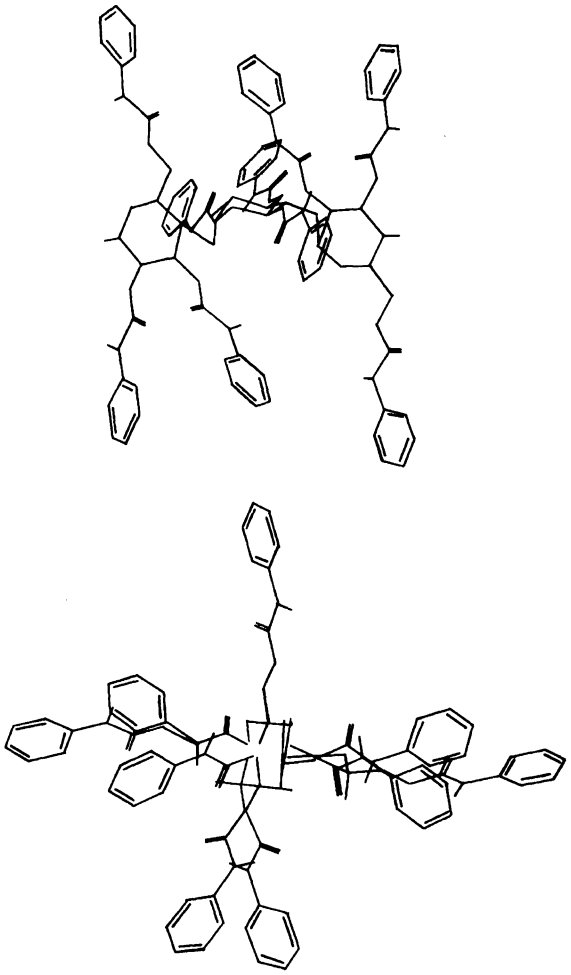


Fig. 9. Structure of amylose tris(phenylcarbamate). Top: along the chain axis; bottom: perpendicular to the chain axis.[10]

Conclusion

The optical resolving abilities of 2,3-bis(3,5-dimethylphenylcarbamate)- 6- (3, 5- dichlorophenylcarbamate) and 2, 3- bis(3, 5- dichlorophenylcarbamate)- 6- (3, 5- dimethylphenylcarbamate) of cellulose and amylose were evaluated. The chiral recognition abilities of the cellulose and amylose derivatives bearing irregularly either the 3,5-dimethylphenyl- or 3,5-dichlorophenylcarbamate group at the 2,3, and 6 positions were also examined. In the cellulose derivatives, the optical resolving ability depended greatly on the kind of racemates, and the carbamate moieties at the 2,3, and 6 positions may complicatedly influence chiral discrimination. On the other hand, in the amylose derivatives, chiral recognition on 2,3-bis(3,5-dimethylphenylcarbamate)-6-(3,5-dichlorophenylcarbamate) was similar to that on tris(3, 5-dimethylphenylcarbamate), and that on 2,3-bis(3,5-dichlorophenylcarbamate)-6-(3,5-dimethylphenylcarba-

mate) was similar to that on tris(3,5-dichlorophenylcarbamate). In the amylose derivatives, chiral discrimination seems to be more influenced by the side groups at the 2 and 3 positions than that at the 6 position. This difference between the cellulose and the amylose derivatives may be ascribed to the difference of their higher-order structures.

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