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OPTICAL RESOLUTION OF AMINO ACID DERIVATIVES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ON TRIS(PHENYLCARBAMATE)S OF CELLULOSE AND AMYLOSE

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SUMMARY

The optical resolution of ten N-protected alanine esters was examined by high-performance liquid chromatography using six cellulose and five amylose tris(phenylcarbamate) derivatives as chiral stationary phases. Tris(3,5-dimethylphenylcarbamate)s of both cellulose and amylose showed high resolving power for these racemates. The resolution of 23 N-benzyloxycarbonyl α-amino acid esters was also tested on tris(3,5-dimethylphenylcarbamate)s of cellulose and amylose. All amino acid derivatives except two were completely resolved at least by one of the colums. On cellulose tris(3,5-dimethylphenylcarbamate), the L-isomers of the amino acids except for threonine were eluted first.

INTRODUCTION

Recently, we reported that phenylcarbamate derivatives of polysaccharides, particularly cellulose tris(phenylcarbamate)s (CTPCs)[1–3] and amylose tris(phenylcarbamate)s (ATCPs)[4], showed characteristic optical resolving abilities for various enantiomers when used as a chiral stationary phase (CSP) for high-performance liquid chromatography (HPLC). The optical resolving abilities of the derivatives having various substituents on the phenyl groups were dependent greatly on the inductive effects of the substituents, and either 3,5-dimethyl- or 3,5-dichlorophenylcarbamates of cellulose and amylose often showed the best chiral recognition abilities for many racemic compounds.

In this work, we investigated the resolution of N-protected amino acid esters by using CTPC (**1–6**) and ATPC (**7–11**) derivatives. The amino groups of racemic amino acids were protected with acetyl (Ac), benzoyl (Bz), *tert.*-butoxycarbonyl (Boc), phenoxycarbonyl (PhOC) or benzyloxycarbonyl (CBZ) groups and the carboxy group with ethyl (Et) or benzyl (Bzl) groups.

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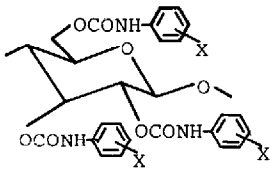
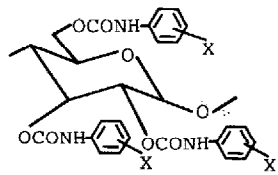


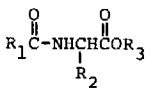
CTPC

	X =
1	3,5-Me_2
2	4-Me
3	4-Et
4	H
5	4-F
6	4-Br

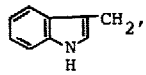


ATPC

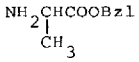
	X =
7	3,5-Me_2
8	4-Me
9	H
10	4-Cl
11	3,5-Cl_2



$R_1 = CH_3$, Ph, $t\text{-}C_4H_9O$, PhO, $PhCH_2O$

$R_2 = CH_3$, C_2H_5, $(CH_3)_2CH$, $CH_3(CH_2)_2$, $(CH_3)_2CHCH_2$, $CH_3(CH_2)_3$, $CH_3CH_2(CH_3)CH$, Ph, $PhCH_2$, $HOCH_2$, $HO(CH_3)CH$, Bzl-O-$C_6H_4CH_2$, R_3OOCCH_2, $R_3OOC(CH_2)_2$, H_2NCOCH_2, $H_2NCO(CH_2)_2$, $HC{=}C{-}CH_2$,  , $CBZ\text{-}NH(CH_2)_4$, $CH_3CH_2SCH_2$,  , $Bzl\text{-}SCH_2$, $-(CH_2)_3-$, $-(CH_2)_4-$

$R_3 = C_2H_5$, $PhCH_2$



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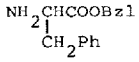

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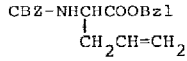

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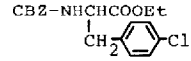

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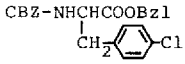

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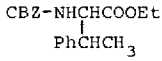

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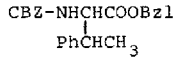

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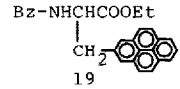

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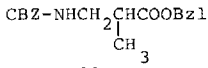

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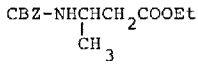

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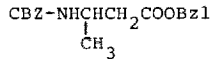

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EXPERIMENTAL

Details on the preparation of CSPs were described previously[2]. CTPC and ATPC derivatives (25%, w/w of silica gel) were adsorbed on macroporous silica gel (Nucleosil 4000-7), which had been treated with 3-aminopropyltriethoxysilane.

Each CSP was packed in a stainless-steel tube (25 cm × 0.46 cm I.D.) by a

slurry method. Chromatographic analyses were performed on a JASCO Trirotar-II chromatograph equipped with UV (JASCO UVIDEC-100-III) and polarimetric (JASCO DIP-181C) detectors. The optical resolution was monitored with a flow cell (50 mm × 2 mm (I.D.) at full lamp (mercury) intensity without a filter. Optical resolution was performed with an hexane–2-propanol mixture at a flow-rate of 0.5 ml min^{-1} at 25°C. The dead time, t_0, was estimated with 1,3,5-tri-*tert.*-butylbenzene as a non-retained compound[5]. ^1H NMR spectra were measured with a JEOL-MH-100 (100 MHz) spectrometer.

Racemic and optically active samples of amino acid derivatives were prepared by the conventional methods and were identified by IR, ^1H NMR and elemental analyses.

RESULTS AND DISCUSSION

Fig. 1 shows the complete resolution of alanine as its N-benzyloxycarbonyl ethyl ester on cellulose tris(3,5-dimethylphenylcarbamate) **1**. The capacity factors, $k'_1 = (t_1 - t_0)/t_0$ and $k'_2 = (t_2 - t_0)/t_0$, for the first and second isomers eluted were 1.56 and 2.82, respectively, and the separation factor, $\alpha = k'_2/k'_1$, which represents the chiral recognition ability of CSPs, was 1.82. The resolution factor, R_s, which can be estimated by $2(t_2 - t_1)/(W_1 + W_2)$, was 4.82.

Ten N-protected alanine esters were chromatographed on CTPC derivatives **1**–**6** (Table I). The chiral recognition abilities of CSPs depended greatly on the substituents of CTPCs. Among the six CTPC derivatives, the 4-bromo derivative **6** exhibited the best resolving power for Ac-Ala-OEt, Ac-Ala-OBzl, Bz-Ala-OBzl, PhOC-Ala-OEt and PhOC-Ala-OBzl. However, these alanine derivatives gave rather broad peaks on **6** as shown by the relatively small R_s values. On the other hand, compound **1** exhibited the highest α and R_s values for N-CBZ alanine derivatives.

Recently, we reported that compound **1** exhibits high optical resolving power for the phenylcarbamates (PhNHCOOR*) of racemic secondary alcohols (R*OH)

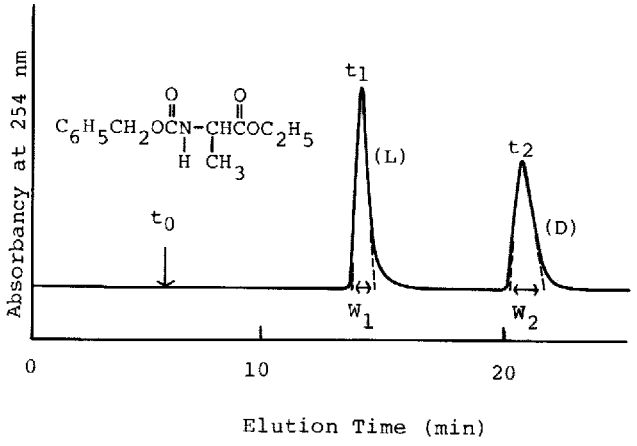

Fig. 1. Chromatographic resolution of N-benzyloxycarbonyl alanine ethyl ester on cellulose tris(3,5-dimethylphenylcarbamate) **1** (Column: 25 cm × 0.46 cm I.D. Eluent: hexane–2-propanol (90:10); flow-rate: 0.5 ml/min. Temperature: 25°C.

TABLE I

RESOLUTION OF N-PROTECTED ALANINE DERIVATIVES ON CTPC DERIVATIVES **1–6**

Eluents: hexane–2-propanol (80:20); for column **1**, hexane–2-propanol (90:10).

Column	*Ac-Ala-OEt*			*Ac-Ala-OBzl*			*Bz-Ala-OEt*		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
1 3,5-Me_2	1.09(+)	1.12		5.52(−)	1.04	0.72	1.51(D)	1.34	2.30
2 4-Me	1.05(−)	1.25	0.78	1.65(−)	1.32	1.28	1.26(L)	1.12	
3 4-Et	0.68(−)	1.49	1.87	1.18(−)	1.58	2.06	0.66(L)	1.29	0.93
4 H	4.74(−)	1.14	0.88	7.69(−)	1.22	1.57	2.01	1.00	
5 4-F	2.08(−)	1.36	1.11	3.11(−)	1.51	1.58	2.62(L)	1.49	1.29
6 4-Br	1.61(−)	1.63	1.20	2.58(−)	1.65	1.61	2.74(L)	1.22	0.91
	Bz-Ala-OBzl			*Boc-Ala-OEt*[a]			*Boc-Ala-OBzl*[a]		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
1	3.52(D)	1.15	1.26	0.88(D)	*ca.* 1		1.89(D)	1.31	2.13
2	2.10(D)	1.25	1.06	0.48(D)	*ca.* 1		0.87(L)	*ca.* 1	
3	1.20(D)	1.23	1.07	0.19(D)	*ca.* 1		0.61(L)	1.07	
4	3.22(D)	1.15		1.13(D)	*ca.* 1		1.21(L)	1.25	0.68
5	3.87(D)	1.32	1.50	0.76(D)	1.21		0.82(L)	1.28	0.92
6	4.98(D)	1.37	1.71	0.69(D)	*ca.* 1		0.58(L)	1.27	
	PhOC-Ala-OEt			*PhOC-Ala-OBzl*			*CBZ-Ala-OEt*		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
1	1.89(D)	1.30	1.98	4.02(L)	1.03		1.56(L)	1.82	4.82
2	1.53(D)	1.20	0.99	2.79(L)	1.33	2.04	1.28(L)	1.32	1.48
3	0.98(D)	1.09		1.64(L)	1.23	2.04	0.95(L)	1.42	1.86
4	1.81(D)	1.12		2.98(L)	1.31	1.09	3.63(L)	1.20	1.02
5	2.10(D)	1.35	1.32	3.36(L)	1.52	1.86	2.68(L)	1.50	0.79
6	2.37(D)	1.46	1.33	3.39(L)	1.62	2.18	4.37(L)	1.05	
	CBZ-Ala-OBzl								
	k'_1	α	R_s						
1	3.08(L)	2.20	7.26						
2	2.11(L)	1.30	1.53						
3	1.57(L)	1.47	2.59						
4	6.13(L)	1.23	1.41						
5	4.66(L)	1.74	1.93						
6	4.36(L)	1.04							

[a] Eluent: hexane–2-propanol (90:10).

but low resolving power for the benzoyl esters (PhCOOR*)[6]. This suggests that the interaction between the urethane groups of (±)-PhNHCOOR* and the urethane groups of **1** is much more important for the resolution than the interaction between the ester group of (±)-PhCOOR* and **1**. Therefore, in the present optical resolution,

the interaction between the N-protecting groups and the urethane groups of CSPs may be more important than that between the ester groups and CSPs. However, the elution order of enantiomers depended greatly on the protecting groups for both the NH_2 and COOH groups. D-Isomers of Bz-Ala-OBzl, Boc-Ala-OEt and PhOC-Ala-OEt were always eluted first regardless of the nature of the CSPs; in the resolution of other derivatives, L-isomers were less strongly retained except in the separations of Bz-Ala-OEt and Boc-Ala-OBzl on **1**. The absolute configurations of the N-acetyl derivates are not clear. The reversed elution order of enantiomers on **1** compared to that on other CTPC derivates has been occasionally recognized[2]. When the protecting group of the amino group was Bz, Boc or PhOC, the elution order of the enantiomers of ethyl esters was mostly opposite to that of benzyl esters. In these separations, the ester groups seem to play an important rôle for chiral recognition. On the other hand, for Ac and CBZ derivates, the difference in the ester groups appears to be less important. In this case, the interaction between CSPs and N-protected groups may be more influential for chiral discrimination than that between CSPs with ester groups. For the ethyl esters, the difference between PhOC and CBZ was important, whereas for the benzyl ester this difference did not affect the elution order of the enantiomers. Boc-Ala esters were weakly retained on the colums compared with other derivatives, and therefore a less polar eluent, hexane–2-propanol (90:10), was used. The Boc group apparently prevents adsorption of the derivatives on the CSPs, which resulted in a low degree of separation.

Table II showed the results of the optical resolution of the ten alanine derivatives on five ATPC derivatives (**7**–**11**). Amylose tris(3,5-dimethylphenylcarbamate) **7** exhibited good resolving power for most alanine derivatives, except for the N-CBZ derivatives. The elution order of the enantiomers of Bz-Ala-OBzl and PhOC-Ala-OEt was mostly reversed compared with that on the CTPC derivates.

The resolution of the ethyl and benzyl esters of 23 N-CBZ α-amino acids was examined on 3,5-dimethylphenylcarbamates **1** and **7** (Table III). Most amino acids, except Phegly and Lys were resolved completely on CTPC derivative **1**. The optical resolving power of compound **7** was low compared with that of **1**. However, Phegly which was not resolved on **1** was completely resolved as its benzyl ester. Lys derivatives were not completely resolved on these columns. Since an additional CBZ group protecting the ε-amino group of Lys exists far from a chiral carbon, the adsorption of this group on CSP may result in low chiral discrimination. On compound **1**, the amino acids where R_2 = alkyl group were better resolved than those where R_2 contained an heteroatom. The adsorption of R_2 on the CSP may disturb the chiral discrimination as in the case of the Lys derivatives. The cyclic amino acids (Pro and pipecolin) were separated with high separation factors. On compound **1**, the L-isomers of all the amino acid derivatives except for CBZ-Thr-OBzl were eluted first. The polar hydroxy group of Thr may be responsible for this exceptional elution order. Many CBZ amino acids with a free carboxy group have been directly resolved on **1** by using hexane–2-propanol containing a small amount of a strong acid like trifluoroacetic acid[7]. In this case, the L-isomers of most amino acids were also eluted first. Therefore, in the resolution of CBZ amino acids and their esters, L-isomers are less strongly retained regardless of the structure of the COOR group of the amino acids. The interaction between the CBZ group and the urethane group of compound **1** appears to govern the chiral discrimination.

TABLE II

RESOLUTION OF N-PROTECTED ALANINE DERIVATIVES ON ATPC DERIVATIVES **7–11**

Eluent: hexane–2-propanol (90:10).

Column	*Ac-Ala-OEt*			*Ac-Ala-OBzl*			*Bz-Ala-OEt*		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
7 3,5-Me_2	0.73(+)	1.53	1.76	2.33(+)	1.37	2.59	1.64(D)	1.43	2.33
8 4-Me	2.93(−)	1.15		3.73(−)	1.24	0.95	3.26	1.00	
9 H	3.19(+)	*ca.* 1		4.12(−)	*ca.* 1		3.58(L)	*ca.* 1	
10 4-Cl	4.11(−)	*ca.* 1		5.53(−)	*ca.* 1		4.18(L)	*ca.* 1	
11 3,5-Cl_2	2.27(−)	1.09	1.01	4.57(+)	1.14	1.06	3.56(D)	*ca.* 1	
	Bz-Ala-OBzl			*Boc-Ala-OEt*			*Boc-Ala-OBzl*		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
7	3.33(D)	1.41	3.27	0.51(L)	*ca.* 1		0.89(L)	1.27	1.17
8	4.69	1.00		0.41(L)	1.09		0.67(L)	1.08	
9	4.16(L)	1.04		0.33(D)	*ca.* 1		0.67(L)	*ca.* 1	
10	3.32(L)	1.10		0.75(L)	*ca.* 1		0.93	1.00	
11	5.25(L)	1.12	1.29	1.04(L)	1.15	1.10	1.77(D)	1.05	
	PhOC-Ala-OEt			*PhOC-Ala-OBzl*			*CBZ-Ala-OEt*		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
7	1.25(L)	1.25	1.41	2.18(L)	1.25	1.95	1.37(L)	*ca.* 1	
8	2.20(L)	1.44	2.29	2.86(L)	1.37	1.70	1.42(L)	*ca.* 1	
9	2.71(D)	1.23	0.74	3.92(L)	1.33	1.02	5.09(L)	*ca.* 1	
10	3.06(L)	*ca.* 1		3.71(L)	1.05		1.80(L)	*ca.* 1	
11	1.81(L)	1.33		3.26(L)	1.05		2.05(L)	1.19	
	CBZ-Ala-OBzl								
	k'_1	α	R_s						
7	2.18(L)	*ca.* 1							
8	2.15(L)	1.11							
9	3.41(L)	1.12							
10	2.19(L)	1.06							
11	4.57(D)	1.14	1.06						

N-Unprotected benzyl esters of Ala (**12**) and Phe (**13**) were not effectively resolved on **1** as compared with the corresponding N-CBZ derivatives (Table IV). This also suggests that the CBZ group may be very important in attaining efficient resolution.

The resolution of other amino acid derivatives (**14–22**) on compound **1** and **7** was also examined (Table IV). Most compounds were completely resolved on either **1** or **7** or on both. The separation factors for β-amino acid derivatives (**20–22**) were smaller than those for structurally similar alanine derivatives. These results indicate

TABLE III

RESOLUTION OF N-CBZ AMINO ACID ESTERS ON COLUMNS 1 AND 7

Eluent: hexane–2-propanol (90:10).

Amino acid	*1*						*7*					
	Et			*Bzl*			*Et*			*Bzl*		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
Ala	1.56(L)	1.82	4.82	3.08(L)	2.20	7.26	1.37(L)	*ca.* 1		2.18(L)	1.03	
Butyline[b]	0.89(L)	2.91	3.07	2.40(L)	3.28	4.68	2.53	1.00		3.86(L)	1.13	
Val	0.89(L)	2.76	6.65	1.51(L)	4.12	9.88	1.89(L)	1.17	0.80	3.19(L)	1.33	1.69
Nva	1.14(L)	1.77	2.70	2.22(L)	2.32	6.73	2.51(L)	1.06		3.65(L)	1.12	0.97
Leu	1.35(L)	1.57	3.34	2.23(L)	1.83	4.46	2.51(D)	1.29	1.19	3.68(L)	1.10	
Nle	1.07(L)	1.40	1.78	1.93(L)	1.64	3.48	2.39(D)	1.09		3.13(L)	1.13	0.79
Ile	0.77(L)	3.10	3.42	1.36(L)	4.03	6.40				3.60(L)	1.48	3.10
Phegly	4.03(D)	*ca.* 1		7.85(L)	1.04		3.55(L)	1.10		6.05(L)	1.25	1.12
Phe	1.41(L)	1.45	1.59	3.61(L)	1.21	1.45	3.97(L)	*ca.* 1		6.01	1.00	
Ser	4.26(L)	1.17	1.35	7.77(D)	*ca.* 1		4.90(D)	1.27	1.47	6.78(D)	1.34	2.81
Thr	3.40(D)	*ca.* 1		5.53(D)	1.37		5.81(L)	1.08		6.92(L)	1.10	
Tyr(OBzl)	2.45(L)	1.33	1.00	4.91	1.00		4.19(L)	1.36	2.16	6.35(L)	*ca.* 1	
Asp	2.35(L)	1.31	1.98	3.12(L)	1.11	0.87	4.15(L)	1.08		5.53(D)	1.10	0.94
Glu[a]	1.38(L)	1.42	1.26	3.35(L)	1.58	1.12	2.07(L)	1.07		5.03(D)	*ca.* 1	
Asn[a]	2.15(L)	1.33	1.69	3.82(L)	1.34	2.77	2.90(D)	1.06		4.46(L)	1.11	0.59
Gln[a]	2.26(L)	1.31	1.39	3.67(L)	1.35	1.63	2.91(L)	*ca.* 1		3.75(D)	1.10	
His[a]	1.35(−)	1.41	2.33				2.87(−)	1.21	0.98			
Trp[a]	2.96(L)	1.50	3.61	4.53(L)	1.55	1.84	2.89(L)	1.14	1.06	4.11(L)	1.19	1.57
Lys(CBZ)[a]	3.19(+)	1.13		5.20(+)	*ca.* 1		6.22(+)	*ca.* 1		8.61(+)	1.14	0.95
Cys(SBzl)	1.60(L)	1.51	1.53	2.82(L)	1.62	2.31	2.69(L)	*ca.* 1		4.21(D)	1.05	
Met	1.07(L)	1.36	1.41	1.38(L)	1.66	4.35	4.40(D)	1.04		8.40(L)	1.11	1.10
Pro	0.91(L)	2.19	1.91	1.81(L)	2.51	4.09	1.89(D)	1.17	0.80	3.33(D)	1.06	
Pip	0.82(L)	1.95	2.54	1.36(L)	2.10	3.18	1.44(D)	1.27		2.25(D)	*ca.* 1	

[a] Eluent: hexane–2-propanol–diethylamine (80:20:0.1).

[b] 2-Aminobutyric acid.

TABLE IV

RESOLUTION OF OTHER AMINO ACID DERIVATIVES **12–22** ON **1** AND **7**

Eluent: hexane–2-propanol (90:10).

Racemate	*1*			*7*		
	k'_1	α	R_s	k'_1	α	R_s
12	1.98(L)	1.20	1.10	1.33(D)	*ca.* 1	
13	2.18(L)	1.17	0.78	2.14(L)	1.11	
14	2.57(−)	2.22	6.40	4.04(−)	1.13	1.31
15	2.45(+)	1.41	2.56	5.03(+)	1.11	1.02
16	4.23(−)	*ca.* 1		7.30(−)	*ca.* 1	
17	1.00(+)	1.70	3.89	2.04(−)	1.08	
18	1.69(−)	1.79	4.09	4.33(+)	1.02	
19	4.31(+)	1.39	3.04	9.01(+)	1.25	
20	1.47(+)	1.08		2.23(−)	1.03	
21	3.20(+)	1.20	0.98	3.13(−)	1.06	
22	3.49(−)	1.06		3.00(−)	1.11	

that the existence of CBZNH and ester groups on the same asymmetric carbon is important to attain effective chiral discrimination.

In order to estimate the electronic effect of N-protecting groups, seven 4-substituted benzoyl alanine benzyl esters were synthesized. Fig. 2 shows the relationship between the separation factors and Hammett's σ constants of the substituents. Good resolutions were attained with the benzoyl derivatives having either electron-donating

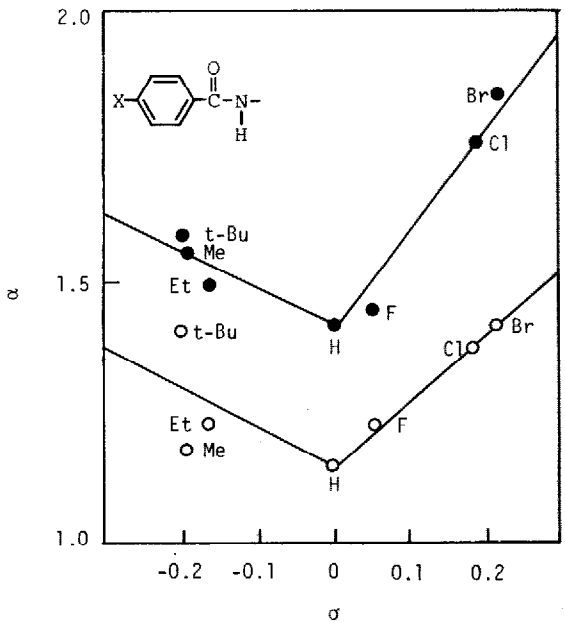

Fig. 2. Plots of the separation factor, α, of N-(4-substituted benzoyl)alanine benzyl esters on columns **1** (○) and **7** (●) against Hammett's σ values.

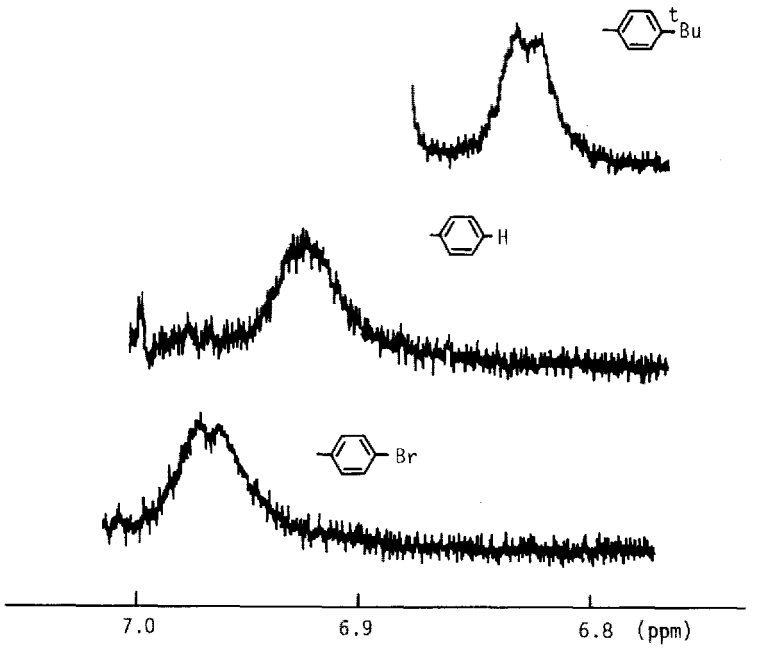

Fig. 3. ^1H NMR spectra of the NH protons of N-(4-substituted benzoyl)alanine benzyl esters (C^2HCl_3, 35°C, relative to tetramethylsilane).

or electron-withdrawing substituents. The unsubstituted N-benzoyl derivative was resolved with the lowest separation factor on these CSPs. Since the substituents themselves on the phenyl group do not seem to interact with the CSPs[2], the changes in the separation factors may be attributed mainly to the change in polarity of the amide bond. The NMR spectra of the –NH proton of 4-substituted benzoyl alanine benzyl esters in C^2HCl_3 are shown in Fig. 3. The NH resonances shift downfield as the electron-withdrawing power of the substituents on the phenyl group increases. This indicates that the acidity of the NH proton increases with increasing electron-withdrawing power of the substituents. The NH proton probably interacts with the CSP through an hydrogen bond formed with the carbonyl oxygen of the CSP (Fig. 4), and

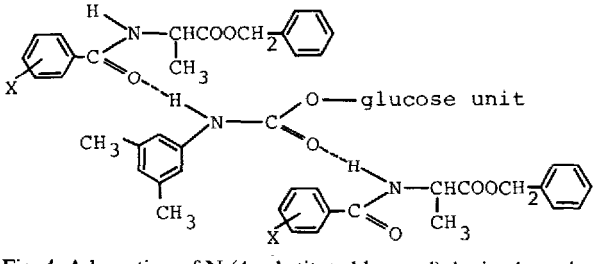

Fig. 4. Adsorption of N-(4-substituted benzoyl)alanine benzyl esters on cellulose tris(3,5-dimethylphenylcarbamate).

therefore this interaction may be more important for the amino acid derivatives having electron-withdrawing substituents. On the other hand, the electron density of the carbonyl oxygen of the alanine derivative, which is also considered to be an important adsorbing site and may interact with the NH proton of the CSP, probably increases with increasing electron-donating power of the substituents. The combination of these factors appears to lead to the results shown in Fig. 2.

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