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Short Communication

2,3,4,6-Tetra-O-benzoyl-β-D-glucopyranosyl isothiocyanate: an efficient reagent for the determination of enantiomeric purities of amino acids, β-adrenergic blockers and alkyloxiranes by high-performance liquid chromatography using standard reversed-phase columns

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ABSTRACT

The use of the chiral derivatization reagent 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl isothiocyanate (BGIT) is described for the conversion of a variety of amino acids and β-adrenergic blockers into diastereomeric thioureas, which can be separated on achiral RP-18 HPLC columns. In comparison with the established reagent 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate (AGIT), BGIT shows increased sensitivity owing to the higher molar absorptivity on the BGIT derivatives. Also a series of monosubstituted alkyloxiranes was transformed with 2-propylamine into the corresponding amino alcohols, which were then further reacted with BGIT, 2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl isothiocyanate (PGIT) or AGIT, leading to the corresponding thiourea derivatives. The diastereomers derived from BGIT could be separated with excellent resolution on a standard RP-18 column, whereas the PGIT and AGIT derivatives showed less or no resolution.

INTRODUCTION

One of the most widely used chiral reagents for the derivatization of enantiomeric amines to form diastereomeric thioureas is 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate (AGIT), introduced by Kinoshita and co-workers [1–3]. As a derivative of natural glucose it is optically pure. The conditions for the derivatizations are mild, thus minimizing possible racemization during the reactions. AGIT has been used for the separation of α-amino acids [1,2,4], amphetamines [5], norepinephrine [3,6], epinephrine [7], propranolol [8], amino alcohols [9,10], mexiletine [11] and oxiranes [12]. It was pointed out by Scott *et al.* [13] and Nambara and co-workers [14,15] that the degree of separation of diastereomers should depend strongly on the rigidity of their conformation and Kinoshita *et al.* [2] suggested that the conformations of their thioureas derived from AGIT and amino acids are rigidly fixed owing to the bulky acetylglycosyl residues. It was to be expected that this effect would be amplified by the introduction of even more bulky benzoyl or pivaloyl groups into the carbohydrate moiety. We therefore decided to investigate whether 2,3,4,6-

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tetra-O-benzoyl-β-D-glucopyranosyl isothiocyanate (BGIT) and 2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosyl isothiocyanate (PGIT) would be suitable for the separation of amino derivatives that can be analysed only with difficulty using AGIT.

Enantiomerically pure, monosubstituted alkyloxiranes are important chiral building blocks for the synthesis of pheromones [16–19], δ-lactones [20–22] and other important naturally occurring compounds [23], and for polyoxiranes [24] and ferroelectric liquid crystals [25–27]. In contrast to oxiranes carrying chromophores (*e.g.*, aromatic substituents), there is no simple and general method available for the determination of their optical purities. Schurig and co-workers described the resolution of methyl- [28–32], ethyl- [29–32], 2-propyl- [29–31], *tert.*-butyl- [30,31] and vinyloxirane [32] using optically active bis[(1*R*)-3-(heptafluorobutyryl)-camphorates] of nickel(II) [28,29,31,32], manganese (II) [30,31] and cobalt(II) [31] as stationary phases in capillary gas–liquid chromatographic columns. Low separation factors (α = 1.02–1.04, resolution data not given) were reported by Li *et al.* [33] in the resolution of *n*-butyl-, *n*-hexyl-, *n*-octyl-, *n*-decyl- and *n*-dodecyloxirane using 2,6-di-O-pentyl-3-O-trifluoracetyl-α-cyclodextrin (DP-TFA-α-CD) as liquid stationary phase in capillary gas chromatography. Better results in the resolution of *n*-butyloxirane were obtained by Li *et al.* [33] using DP-TFA-γ-CD (α = 1.10) and König [34] employing a modified β-cyclodextrin. The best results so far were obtained by Gal [12] employing a two-step derivatization procedure involving ring opening of the corresponding oxiranes (methyl-, *tert.*-butyl- and *n*-hexyloxirane) using a variety of primary amines, followed by derivatization of the resulting amino alcohols with AGIT. The obtained separation factors (α = 1.15–1.23) and resolutions (R_s = 2.14–2.29) are acceptable. Unfortunately, the times required for the first derivatization step using cyclohexylamine [68 h], *n*-butylamine [24 h] and isobutylamine [2 h] are frequently much too long.

In order to facilitate the whole procedure and reduce the times required for derivatization we chose 2-propylamine for the ring opening of the oxiranes. Using this procedure the time required for the preparation of amino alcohols is only 2 h. Results obtained in the resolution of the oxirane-derived amino alcohols were compared using BGIT, PGIT and AGIT as reagents for the second derivatization step.

In addition to improved resolutions due to increased steric bulk (benzoate and pivaloate *versus* acetate), it was expected that the use of BGIT derivatives would result in higher detection sensitivities for the resulting diastereomeric thioureas as compares with AGIT. Therefore, the UV absorbance spectra of BGIT, AGIT and their thiourea derivatives of L-leucine were recorded and compared.

In order to demonstrate the versatile applicability of BGIT, it was also used for the separation of β-adrenergic blockers and a variety of natural and unnatural amino acids.

EXPERIMENTAL

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide, 2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosylamine, thiophosgene, 1,2-alkenes, racemic oxiranes, (*R*)-(+)-methyloxirane, amino acids, β-adrenergic blockers and other reagents including 67 m*M* phosphate buffer (pH 7.0) were obtained from Aldrich, Fluka, Lancaster and Merck. Racemic *n*-propyl-, *n*-pentyl- and *n*-heptyloxirane were synthesized from the corresponding 1,2-alkenes according to the procedure of Terao *et al.* [35]. Enantiomerically pure oxiranes except (*R*)-(+)-methyloxirane were synthesized via the enzymatic route reported by Goergens and Schneider [36]. BGIT and AGIT were prepared by treatment of 2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl bromide and 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide with silver thiocyanate according to the procedure of Van de Kamp and Micheel [37]. 2,3,4,6-Tetra-O-benzoyl-α-D-glucopyranosyl bromide was prepared from D-glucose in two steps as described by Ness *et al.* [38]. PGIT was prepared by treatment of 2,3,4,6-tetra-O-pivaloyl-β-D-galactopyranosylamine with thiophosgene according to the procedure of Fuentes Mota *et al.* [39]. AGIT, BGIT and PGIT are also commercially available from Fluka (product numbers 86550, 86729 and 88102, respectively).

Equipment

The UV absorbance spectra were recorded with a UV-160A UV–Vis recording spectrophotometer (Shimadzu). The chromatographic system consisted

of an L-6200 intelligent pump (Merck–Hitachi), L-4200 UV–Vis Detector (Merck–Hitachi), D-2500 chromato-integrator (Merck–Hitachi) and a LiChrospher 100 RP-18 column (25 × 4 mm I.D., particle size 5 μm) (Merck). An L-6210 intelligent pump (Merck–Hitachi) was used if the mobile phase contained phosphate buffer.

Derivatization of amino acids and β-adrenergic blockers

A 5-mg amount of the corresponding amino acid or 0.1 mmol of the β-adrenergic blocker was dissolved in 50% (v/v) aqueous acetonitrile containing 0.55% (v/v) triethylamine in order to give a final volume of 10 ml. To 50 μl of this stock solution 50 μl of 0.66% (w/v) BGIT in acetonitrile were added. The resulting mixture was shaken on a laboratory shaker for 30 min, then 10 μl of 0.26% (v/v) ethanolamine in acetonitrile were added and shaking was continued for another 10 min. Ethanolamine reacts with any excess of BGIT and the resulting thiourea derivative is eluted well behind any of the amino acid derivatives. The mixture was then diluted with acetonitrile to a final volume of 1 ml and a 10-μl aliquot was used for HPLC.

Derivatization of oxiranes

Aliquots of 50 μl of the oxiranes were placed in 1-ml vials, to which 200 μl of 2-propylamine were added. The vials were tightly closed with a Teflon-lined cap and heated at 100°C for 2 h. Excess of 2-propylamine was evaporated in a stream of air, 950 μl acetonitrile were added and 50-μl aliquots were placed in a 1-ml Eppendorf vial. A 50-μl volume of 0.66% (w/v) BGIT, 0.56% (w/v) PGIT or 0.4% (w/v) AGIT in acetonitrile was added and the mixtures were allowed to stand at room temperature for 30 min. The resulting mixtures were diluted with acetonitrile to a final volume of 1 ml and a 7-μl aliquot was used for HPLC.

RESULTS

AGIT shows maximum UV absorption at 250 nm (π–π^* transition of the carbon–sulphur double bond), whereas BGIT has a maximum absorption at 231 nm (π–π^* transition in the benzoyl groups). The maximum molar absorptivity of BGIT is 60 times higher than that of AGIT (Table I). After derivatization with an α-amino acid (L-leucine), the molar absorptivity of the BGIT thiourea derivative decreases slightly in comparison with the underivatized reagent. In contrast, the corresponding thiourea derivative of AGIT displays a molar absorptivity ten times higher than that of AGIT itself, owing to the formation of the thiourea group (Table I). In summary, molar absorptivities of BGIT thiourea derivatives are about five times higher than those of AGIT thiourea derivatives.

TABLE I

MOLAR ABSORPTIVITIES OF BGIT, AGIT AND THEIR THIOUREA DERIVATIVES OF L-LEUCINE AT THEIR WAVELENGTHS OF MAXIMUM ABSORPTION

Absorbances were measured at concentrations between 10^{-5} and 10^{-4} mol/l in acetonitrile; λ_{max} = wavelength of maximum absorption; ε (λ_{max}) = molar absorptivity at λ_{max}.

Compound	λ_{max} (nm)	$\varepsilon(\lambda_{max})$ (l mol^{-1} cm^{-1})
BGIT	231	$5.79 \cdot 10^4$
AGIT	250	$9.57 \cdot 10^2$
BGIT–L-leucine	231	$5.05 \cdot 10^4$
AGIT–L-leucine	250	$1.03 \cdot 10^4$

Seventeen chiral amino acids (eleven natural and six non-natural) and seven β-adrenergic blockers were derivatized using BGIT. With the exception of adrenaline, conditions were found that allowed complete baseline separation of the corresponding diastereomers. Also mixtures of α-amino acids can be analysed and an example of the simultaneous

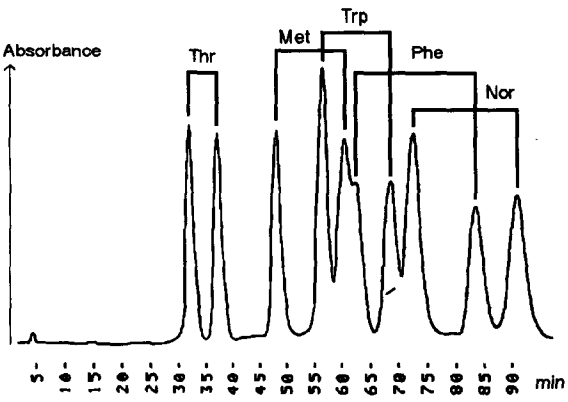

Fig. 1. Separation of ten diastereomeric thiourea derivatives formed from amino acids with BGIT. Mobile phase, methanol–water–67 m*M* phosphate buffer (pH 7.0) (68:27:5); flow-rate, 0.45 ml min^{-1}; 2 nmol of each derivative were injected.

TABLE II

SEPARATION OF DIASTEREOMERIC THIOUREA DERIVATIVES FORMED BY DERIVATIZATION OF RACEMIC AMINO ACIDS WITH BGIT

Column: LiChrospher 100 RP-18 (5 μm). Conditions: (A) mobile phase = methanol–water–67 m*M* phosphate buffer (pH 7.0) (65:27:8), flow-rate = 0.42 ml min^{-1}, t_0 = 4.1 min; (B) mobile phase = methanol–water–67 m*M* phosphate buffer (pH 7.0) (70:25:5), flow-rate = 0.45 ml min^{-1}, t_0 = 3.7 min; (C) mobile phase = methanol–water–67 m*M* phosphate buffer (pH 7.0) (80:15:5), flow-rate = 0.50 ml min^{-1}, t_0 = 3.1 min. k', α and R_s are defined in the text.

Amino acid	k'_L	k'_D	α	R_s	Conditions
Alanine	18.00	20.85	1.16	2.72	A
Isoleucine	9.27	12.35	1.33	3.08	B
Leucine	9.51	12.65	1.33	3.74	B
Lysine	13.48	15.32	1.14	2.28	C
Methionine	8.08	10.24	1.27	4.55	B
Phenylalanine	10.54	13.81	1.31	4.84	B
Proline	6.41	5.19	1.23	2.50	B
Threonine	5.35	6.24	1.17	2.28	B
Tryptophan	9.43	12.03	1.27	4.36	B
Tyrosine	6.22	7.41	1.19	2.00	B
Valine	7.22	9.16	1.27	3.00	B
2-Aminobutyric acid	6.24	7.57	1.21	2.97	B
3-Aminobutyric acid	16.88	18.95	1.12	2.74	A
Norleucine	12.89	16.81	1.30	5.92	B
Ornithine	11.94	13.90	1.16	2.54	C
Penicillamine	7.37	10.05	1.33	4.00	B
Phenylglycine	6.38	7.86	1.23	2.20	B

analysis of five racemic amino acids is shown in Fig. 1. Retention and resolution parameters of the diastereomeric BGIT derivatives are given in the Tables II and III (k', α and R_s refer to the capacity factor, separation factor and resolution, respectively, for a given pair of diastereomers).

Also thirteen monosubstituted racemic alkyloxiranes were converted with 2-propylamine into the

TABLE III

SEPARATION OF DIASTEREOMERIC THIOUREA DERIVATIVES FORMED BY DERIVATIZATION OF RACEMIC β-ADRENERGIC BLOCKERS WITH BGIT

Column: LiChrospher 100 RP-18 (5 μm). Conditions: (A) mobile phase = methanol–water (70:30), flow-rate = 1 ml min^{-1}, t_0 = 1.55 min; (B) mobile phase = methanol–water (80:20), flow-rate = 1 ml min^{-1}, t_0 = 1.55 min; (C) mobile phase = methanol–water (85:15), flow-rate = 0.5 ml min^{-1}, t_0 = 3.1 min; (D) mobile phase = methanol–water (90:10), flow-rate = 0.5 ml min^{-1}, t_0 = 3.1 min. k'_1 = capacity factor of the faster eluting derivative: α and R_s are defined in the text.

β-Adrenergic blocker	k'_1	k'_2	α	R_s	Conditions	Configuration of amine yielding faster eluting BGIT derivative
Adrenaline	22.61	25.67	1.14	1.44	A	
Phenylephrine	33.96	40.07	1.18	3.16	A	*S*
5-(2-N-Benzylamino-2-hydroxyethyl)salicylamide	8.86	11.66	1.32	2.72	B	
Atenolol	5.68	6.66	1.17	2.17	B	
Sotalol	5.01	6.53	1.30	5.88	B	
Pindolol	3.00	3.71	1.24	3.16	C	
Propranolol	2.65	3.65	1.38	4.43	D	

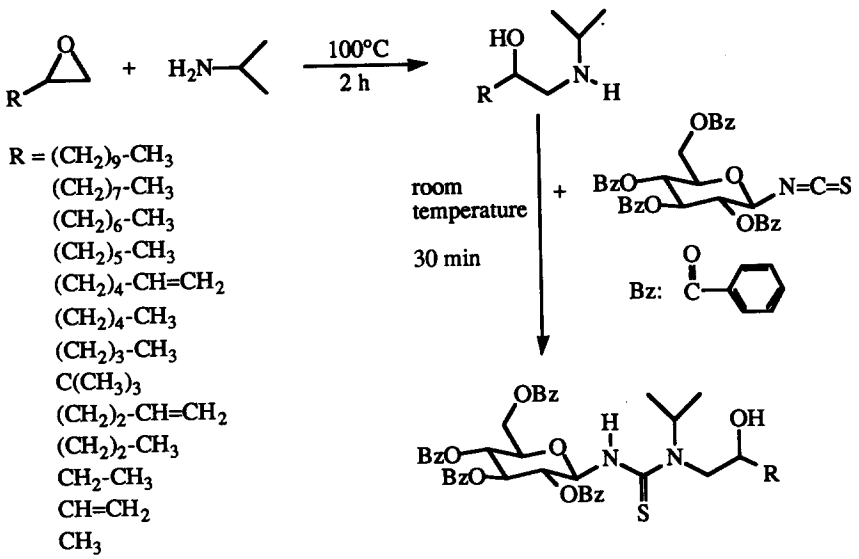

Fig. 2. Derivatization sequence using 2-propylamine and BGIT.

corresponding amino alcohols, which were then derivatized with BGIT, PGIT or AGIT, leading to the corresponding thioureas. The chromatographic analysis was carried out on an RP-18 column with detection at 231 nm (BGIT derivatives) or 250 nm (PGIT and AGIT derivatives).

Retention and resolution parameters of the diastereomeric BGIT, PGIT and AGIT derivatives are summarized in Tables IV–VI. As shown in Table IV and demonstrated in Fig. 3, all diastereomeric BGIT derivatives could be resolved very well and with short retention times. Baseline separations

TABLE IV

SEPARATION OF DIASTEREOMERIC BGIT DERIVATIVES OBTAINED FROM OXIRANE-DERIVED β-AMINO ALCOHOLS

Column: LiChrospher 100 RP-18 (5 μm); flow-rate = 0.50 ml min^{-1}; t_0 = 3.1 min; wavelength of detection = 231 nm. R = substituent as described in Fig. 2. k', α and R_s are defined in the text.

R	Mobile phase (MeOH–H_2O)	k'_R	k'_S	α	R_s	Mobile phase (MeOH–H_2O)	k'_R	k'_S	α	R_s
$(CH_2)_9CH_3$	90:10	9.38	11.35	1.21	4.34	95:5	3.16	3.62	1.15	4.70
$(CH_2)_7CH_3$	90:10	5.58	6.71	1.20	3.51	95:5	1.91	2.17	1.14	2.70
$(CH_2)_6CH_3$	90:10	4.17	5.00	1.20	3.66					
$(CH_2)_5CH_3$	90:10	3.06	3.63	1.19	2.92					
$(CH_2)_4CH=CH_2$	90:10	2.52	2.95	1.17	2.66	85:15	6.99	8.77	1.26	4.62
$(CH_2)_4CH_3$	90:10	2.62	3.06	1.17	2.30	85:15	7.10	8.88	1.25	4.26
$(CH_2)_3CH_3$	90:10	2.19	2.54	1.16	2.16	85:15	5.53	6.83	1.24	4.03
$C(CH_3)_3$	90:10	2.77	2.43	1.14	1.75	85:15	5.29	4.51	1.17	3.01
$(CH_2)_2CH=CH_2$	90:10	1.92	2.23	1.16	1.58	85:15	4.47	5.53	1.24	3.64
$(CH_2)_2CH_3$	90:10	1.96	2.27	1.16	1.58	85:15	3.71	4.50	1.21	3.27
CH_2CH_3	90:10	1.60	1.82	1.14	1.36	85:15	3.46	4.16	1.20	2.73
$CH=CH_2$	90:10	1.55	1.78	1.15	1.73	85:15	3.14	3.78	1.20	2.86
CH_3	90:10	1.45	1.65	1.14	1.55	85:15	2.57	3.06	1.19	2.55

TABLE V

SEPARATION OF DIASTEREOMERIC PGIT DERIVATIVES OBTAINED FROM OXIRANE-DERIVED β-AMINO ALCOHOLS

Column: LiChrospher 100 RP-18 (5 μm); flow-rate = 0.50 ml min^{-1}; t_0 = 3.1 min; wavelength of detection = 250 nm. R = substituent as described in Fig. 2. k', α and R_s are defined in the text.

R	Mobile phase (MeOH–H_2O)	k'_R	k'_S	α	R_s
$(CH_2)_9CH_3$	90:10	17.05	19.41	1.14	2.92
$(CH_2)_7CH_3$	90:10	9.18	10.37	1.13	2.45
$(CH_2)_6CH_3$	90:10	7.06	7.95	1.13	1.97
$(CH_2)_5CH_3$	90:10	5.85	6.50	1.11	1.85
$(CH_2)_4CH=CH_2$	90:10	4.39	4.86	1.11	1.83
$(CH_2)_4CH_3$	90:10	4.73	5.23	1.11	1.73
$(CH_2)_3CH_3$	90:10	3.72	4.03	1.08	1.37
$C(CH_3)_3$	90:10	4.35	3.92	1.11	1.64
$(CH_2)_2CH=CH_2$	90:10	2.95	3.17	1.07	0.96
$(CH_2)_2CH_3$	90:10	2.92	3.10	1.06	0.73
CH_2CH_3	90:10	2.61	2.76	1.06	0.69
$CH=CH_2$	90:10	2.20	2.39	1.09	0.98
CH_3	90:10	2.17	2.28	1.05	–

were achieved in all instances. Owing to the widely different retention times, it was possible to analyse a mixture of five different racemic oxiranes (corresponding to ten diastereomers) in a single experiment (Fig. 3). In contrast less or unsatisfactory separations were observed when PGIT was used as reagent for the second derivatization step (Table V). No or unsatisfactory separations were observed if AGIT was used for derivatization (Table VI).

TABLE VI

SEPARATION OF DIASTEREOMERIC AGIT DERIVATIVES OBTAINED FROM OXIRANE-DERIVED β-AMINO ALCOHOLS

Column: LiChrospher 100 RP-18 (5 μm); flow-rate = 0.50 ml min^{-1}; t_0 = 3.1 min; wavelength of detection = 250 nm, R = substituent as described in Fig. 2. k', α and R_s are defined in the text.

R	Mobile phase (MeOH–H_2O)	k'_R	k'_S	α	R_s
$(CH_2)_9CH_3$	85:15	5.19	5.54	1.07	1.33
$(CH_2)_7CH_3$	85:15	2.78	2.96	1.06	0.92
$(CH_2)_6CH_3$	85:15	2.04	2.16	1.06	–
$(CH_2)_5CH_3$	85:15	1.57	1.66	1.06	–
$(CH_2)_4CH=CH_2$	85:15	1.19	1.25	1.05	–
$(CH_2)_4CH_3$	85:15	1.25	1.30	1.04	–
$(CH_2)_3CH_3$	85:15	1.01	1.01	–	–
$C(CH_3)_3$	85:15	0.99	0.99	–	–
$(CH_2)_2CH=CH_2$	85:15	0.86	0.86	–	–
$(CH_2)_2CH_3$	85:15	0.80	0.80	–	–
CH_2CH_3	85:15	0.68	0.68	–	–
$CH=CH_2$	85:15	0.64	0.64	–	–
CH_3	85:15	0.59	0.59	–	–

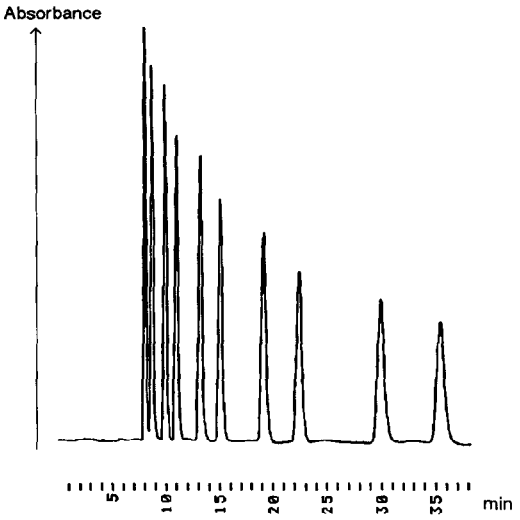

Fig. 3. Separation of a mixture of ten oxirane-derived β-amino alcohols as diastereomeric thiourea derivatives in a single experiment. Mobile phase, methanol–water (90:10); flow-rate, 0.50 ml min^{-1}; 0.7 nmol of each derivative was injected. Components were eluted in the following order: (*R*)-ethyloxirane, (*S*)-ethyloxirane, (*R*)-butyloxirane, (*S*)-butyloxirane, (*R*)-hexyloxirane, (*S*)-hexyloxirane, (*R*)-octyloxirane, (*S*)-octyloxirane, (*R*)-decyloxirane and (*S*)-decyloxirane.

DISCUSSION

The described methods using BGIT as derivatization reagent are very suitable for the determination of enantiomeric purities of chiral amines. BGIT can be prepared easily in optically pure form. It reacts readily with primary and secondary amines under mild conditions without the formation of undesirable by-products. Derivatizations are easy to carry out and separations can be achieved on normal, inexpensive reversed-phase HPLC columns. Owing to the high molar absorptivities of BGIT derivatives small enantiomeric impurities can easily be detected.

The separations achieved for amino acids and β-adrenergic blockers are comparable to the results obtained by Kinoshita *et al.* [2] and Sedman and Gal [10] using AGIT for derivatization. In contrast to AGIT, however, excellent results were obtained in the analysis of amino alcohols derived from chiral alkyloxiranes using BGIT. The method proved to be an excellent tool for the determination of enantiomeric purities in numerous representatives of this class of molecule, regardless of the chain length of the alkyl substituents. Moreover, the described procedure is simple and rapid and the times required for derivatization are greatly reduced in comparison with previous methods.

The assumption that there is a strong relationship between the bulkiness of the derivatization agent and the quality of resolution was not confirmed. In fact PGIT, containing the most bulky pivaloyl groups, did not turn out to induce the best separations, which were achieved using BGIT. Nevertheless, using PGIT the observed resolutions were satisfactory ($R_s > 1.6$) for the determination of enantiomeric purities in seven out of thirteen cases, whereas none of the AGIT derivatives was resolved satisfactorily.

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