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Separation of Enantiomeric Amino Acid Derivatives on Axially Chiral 1,1'-Binaphthyl-2,2'-bis(*N*-decylcarboxamide) as a Stationary Phase for Capillary Gas Chromatography

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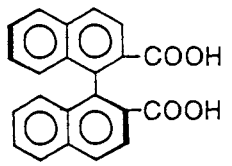
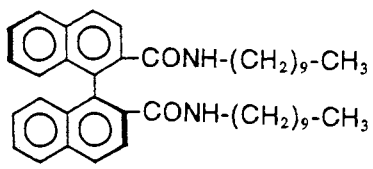
Axially chiral 1,1'-binaphthyl-2,2'-bis(*N*-decylcarboxamide) was utilized as a chiral stationary phase for capillary gas chromatograpic separation of enantiomers. This stationary phase showed efficient differentiation for amino acid derivatives allowing complete separation of eleven *N*-trifluoroacetyl amino acid isopropyl esters.

A variety of chiral stationary phases (CSPs) have been developed for direct separation of enantiomers by gas chromatography.[1,2] Almost all of these CSPs utilize *C*-centrochiral component as the chiral selector. On the other hand, we have reported previously that the chiral stationary phases prepared from axially chiral 1,1'-binaphthyl-2,2'-dicarboxylic acid (**1**) efficiently differentiate enantiomers such as amino acids, amines and alcohols by HPLC.[3,4] Herein, we wish to report the first example to utilize the axially chiral binaphthyl skeleton as the stereodifferentiating element for the gas chromatographic separation of enantiomers.

The stationary phase was prepared as follows. Optically pure (*S*)-**1**[5] was treated with thionyl chloride and then reacted with decylamine in benzene to give 1,1'-binaphthyl-2,2'-bis(*N*-decylcarboxamide) (*S*)-**2**[6] which was purified by silica-gel chromatography. A glass capillary column (26 m x 0.25 mm I.D.) was leached with 6 M HCl at 170 °C, deactivated with barium carbonate and statically wall-coated with a dichloromethane solution of (*S*)-**2** (0.12% W/V) and a commercial silicone oil (OV-17) (0.08% W/V).[7] Samples of racemic amino acids (10 mg) were esterifid in isopropanol saturated with HCl and then acylated with trifluoroacetic anhydride in diethyl ether in the presence of triethylamine to form the *N*-TFA amino acid isopropyl esters, which were washed with water and subjected to the gas chromatographic analysis.



(S)-1



(S)-2

Eleven varieties of amino acids were examined and results of separation are summarized in Table 1. Figure 1 shows a chromatogram of the separation of those amino acid derivatives, recorded in 90 min by programming the temperature from 70 to 130 °C. The *L*-enantiomers are eluted faster except that of proline which has ring structure and lacks amide hydrogen. As is suggested in the separation of enantiomers by chiral amide stationary phases derived from amines or amino acids,[1,2] stereoselective hydrogen bonding between the amide group of *N*-TFA amino acid isopropyl ester and (*S*)-**2** may play an important role for the chiral recognition. Studies on the separation of enantiomeric alcohols, amines, lactones and the like by use of (*S*)-**2** coated column are now under way.

Table 1. Separation factors (α) of *DL*-amino acid derivatives[a)]

Amino acid	α	Col. temp/°C
Ala	1.050	60
Val	1.053	70
allo-Ile	1.039	80
Ile	1.033	80
Nva	1.055	90
Leu	1.047	90
Nle	1.050	90
Pro	1.016	90
Phgly	1.015	120
Glu	1.026	120
Phe	1.041	120

a) Carrier gas, helium at 1.0 atm.

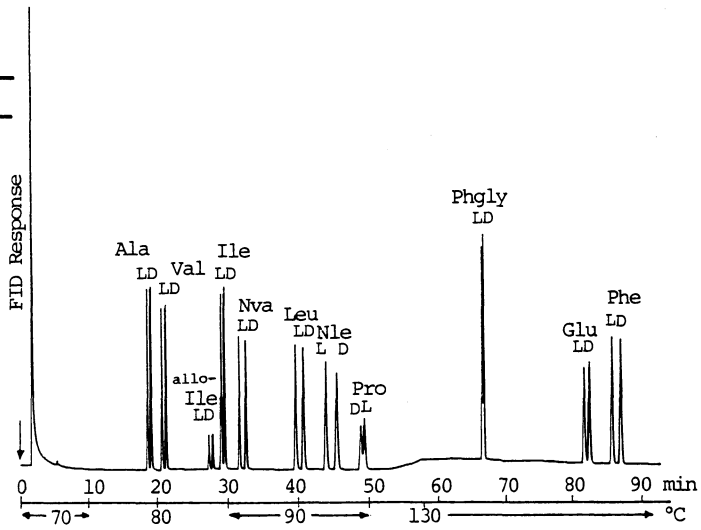


Fig. 1. Separation of *DL*-amino acid derivatives.

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6) Highly viscous liquid, $[\alpha]_D^{20}$ -117.4° (*c* 1.01, acetone).
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