Optical Resolution of Pyridoxal-like Pyridinophanes

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Racemic modifications of the pyridoxal-like ansa compounds such as 15-formyl-14-hydroxy-2,8-dithia-[9](2,5)pyridinophanes prepared as a pontential catalyst for stereospecific nonenzymatic reactions were optically resolved through formation of Schiff bases by treatment with amino sugar derivatives or amino acids. Resolutions with the amino sugar derivatives were ascribable to the difference of the solubilities of the diastereomeric Schiff bases, whereas those with the amino acids resulted from the difference of the reaction rates for the formation of the diastereomeric Schiff bases. As the amino sugar resolving agents, 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-β-D-idofuranose and the corresponding α-D-glucofuranose isomer were employed and gave (*R*)- and (*S*)-pyridoxal-like pyridinophanes, respectively. On the other hand, chiral valine was the most efficient resolving agent among the amino acid tested and the presence of half equimolar Fe^{3+} markedly increased the optical purities of the products. Employment of (*S*)-valine gave (*R*)-pyridinophanes in excess and *vice versa*.

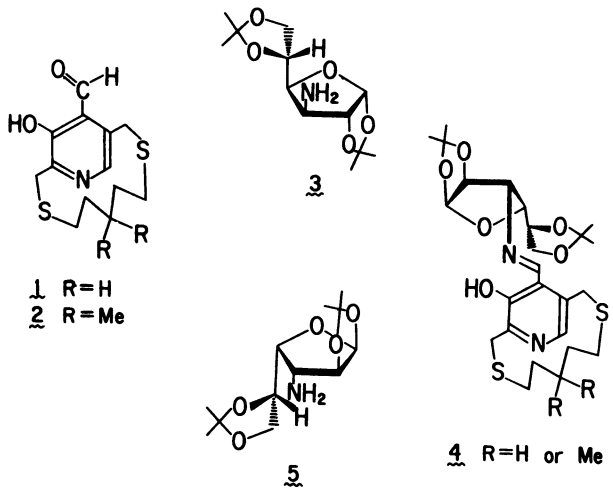
In a series of studies pursuing systems mimicking vitamin B_6-dependent enzymes capable of enantio-face differentiation, we have reported the synthesis of pyridoxal-like pyridinophanes with planar chirality due to restricted rotation; *i.e.*, (*S*)-15-formyl-14-hydroxy-2,8-dithia[9](2,5)pyridinophane ((*S*)-**1**)[1] and (*S*)-15-formyl-14-hydroxy-5,5-dimethyl-2,8-dithia-[9](2,5)-pyridinophane ((*S*)-**2**).[2] Compound (*S*)-**1** was an active catalyst for the stereospecific racemization of a chiral amino acid[1] and both (*S*)-**1** and (*S*)-**2** were important precursors of the corresponding chiral pyridoxamine-like pyridinophanes,[2,3] which played a main role in the stereoselective transamination reactions.[4]

We now wish to describe some interesting additional findings concerning the optical resolutions of the racemate of these pyridoxal-like pyridinophanes. Amino sugar derivatives or amino acids could be employed as the resolving agents but their resolution mechanisms were completely different.

Results and Discussion

Resolution with Amino Sugar Derivatives. As described in the previous paper,[1] the attempt to resolve racemic **1** *via* formation of a Schiff base by treatment with commercial chiral α-methylbenzylamine failed because the Schiff base resisted crystallization; whereas 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**3**) served as an efficient resolving agent for racemic **1**[1] or **2**[2] because it gave a crystalline Schiff base mixture (**4**), from which one diastereomer could be readily isolated in a pure state by recrystallization. Acidic hydrolysis of the less soluble diastereomer gave levorotatory **1** or **2** that was later assigned as the *S*-enantiomer on the basis of X-ray analyses[5] and other data on ORD and CD spectra.[2]

One of the disadvantages of using the amino sugar derivatives such as **3** as the resolving agent was the inaccessibility to its antipode, L-glucofuranose derivative (**5**). This meant that the *R*-enantiomer of the pyridinophanes could not be readily obtainable in a pure state. This situtation prompted us to develop more readily accessible resolving agent in the place of **5**. As a result, 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-D-idofuranose (**6**) proved to be a good candidate. The only difference between **5** and **6** is the configuration of the substituent at C-5 and, therefore, their approximate molecular shapes are quite similar. The preparation of **6** was performed *via* the corresponding 3-azido-3-deoxy derivative (**7**) from the known 1,2:5,6-di-*O*-isopropylidene-β-D-talofuranose (**8**).[6] Thus, **8** was methylsulfonylated at 0 °C to the syrupy 3-*O*-mesylate (**9**), which was treated with sodium azide in hexamethylphosphoric triamide to give the crystalline 3-azido-3-deoxy-D-idofuranose derivative (**7**). The azido sugar derivative was catalytically hydrogenated with Raney Ni, giving **6**. Optical resolution of racemic **1** using **6** was conducted in a similar way to the resolution using **3** reported previously. A mixture of racemic **1** and **6** was refluxed in benzene with azeotropic removal of the water produced, giving a Schiff base mixture (**10**) as crystals. Recrystallization of **10** from a benzene-cyclohexane mixture was conducted twice, giving the less soluble diastereomer (**10a**) of sharp melting



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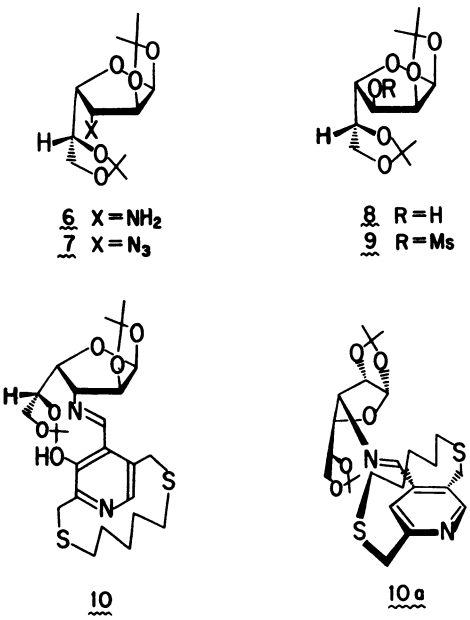


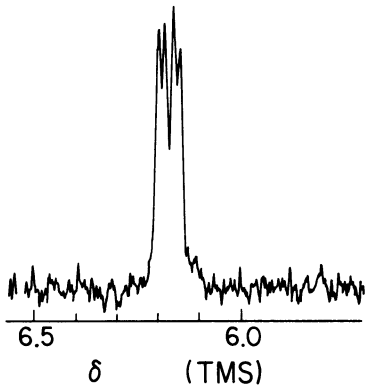
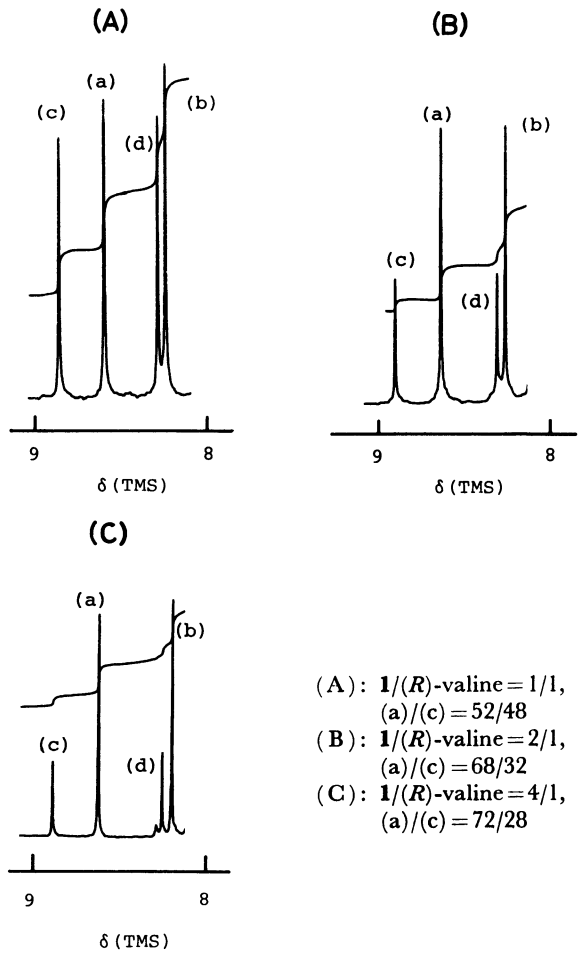


Fig. 1. ^{1}H 100-MHz NMR spectrum of **10**. Signals are anomeric protons of sugar moiety of **10**.

point (150 °C). There was a couple of doublets around δ 6.17 assignable to the anomeric proton of the sugar moiety in the ^{1}H NMR spectrum of **10** as shown in Fig. 1, whereas one doublet at δ 6.18 completely disappeared in the spectrum of **10a**, suggesting that separation between the two diastereomers had been attained. In contrast to the Schiff base isolatable in a homogeneous state from the diastereomeric mixture (**4**, R=H)[1] prepared from **1** and **3**, the crystals of **10a** incorporated 2/3 equimolar benzene and 1/2 equimolar cyclohexane; this was suggested by the results of elemental analyses and the ^{1}H NMR spectra. After acidic hydrolysis of **10a**, the regenerated pyridinophane was extracted with an organic solvent and purified by chromatography, giving the dextrorotary species ((*R*)-**1**) as expected. The absolute value of the specific rotation of this specimen was a little lower than that of the alternative enantiomer previously obtained by using **3** as the resolving agent. This was probably because the *gluco* configuration was superior to the *ido* configuration for the resolution of racemic **1** and since the solubility of **10** was too low to provide smooth fractional crystallization. However, it was interesting that the D-idose derivative (**6**) could substitute the antipode of **3** having the L-*gluco* configuration (**5**). This suggests that optical resolution of atropisomers might depend on the approximate molecular shape of the resolving agent.

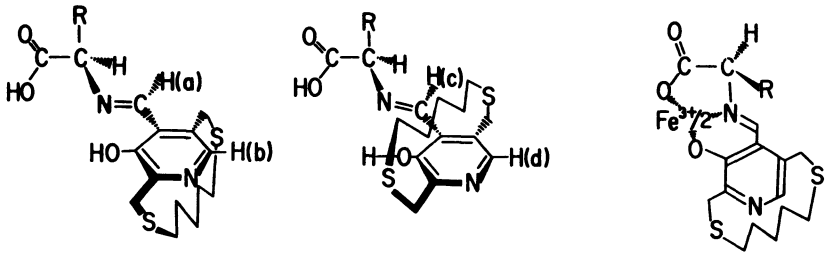
Althouth both enantiomers of pyridoxal-like pyridinophanes could be obtained by employing the **3** and **6** pair as the resolving agents, there was still a problem; *i.e.*, acidic hydrolysis of the Schiff base including the moieties of **3** or **6** for reproduction of the pyridoxal-like pyridinophanes accompanied hydrolysis of the isopropylidene groups in **3** or **6**, making their recovery difficult. These facts further prompted us to develop other type of resolution method.

Resolution with Amino Acids. Generally, pyridoxal and its analogs can condense with free amino acids owing to their great tendency to form Schiff bases.[7,8] As amino acids belong to the most readily obtainable chiral compounds, it would be convenient if they could be utilized for the optical resolu-



(A): **1**/(*R*)-valine=1/1, (a)/(c)=52/48
(B): **1**/(*R*)-valine=2/1, (a)/(c)=68/32
(C): **1**/(*R*)-valine=4/1, (a)/(c)=72/28

Fig. 2. ^{1}H 400-MHz NMR spectra of C_6D_6 solution of the Schiff bases derived from **1** and (*R*)-valine in various molar ratios in methanol. (A): **1**/(*R*)-valine=1/1, (B): **1**/(*R*)-valine=2/1, (C): **1**/(*R*)-valine=4/1. The signals (a—d) are; (a), (c): azomethine protons of **11** and **12**, (b), (d): 6-H protons of pyridine ring of **11** and **12**, respectively.



tion of racemic **1** or **2**. The problem is that racemization of the amino acid moieties may proceed within such Schiff bases, especially when some heavy metal ions are coexisting and the media is basic.[9,10] Therefore, we first examined the capability of the resolution of racemic **1** and **2** with chiral amino acids in the absence of metal ions in neutral media. Racemic **1** was condensed with (*R*)-valine[11] in methanol, changing the molar ratio of both reactants. Figure 2 shows 400 MHz ^{1}H NMR spectra of the C_6D_6 solution of the resulted mixture. Two pairs of signals, (a), (b) and (c), (d), were assigned to the azomethine and pyridine ring protons of the Schiff bases (**11** and **12**) derived from (*S*)-**1** and (*R*)-**1** respectively by referring them to those in the spectra of the Schiff bases derived from the authentic chiral pyridoxal-like pyr-

Table 1. Optical resolution of **1** and **2** with chiral amino acids in the absence of Fe^{3+}

Pyridoxal analog	Amino acid (confign.)	**1** or **2** / Amino acid	Product		
			Confign.[a]	o.p./%[b]	c.y./%[c]
1	Valine (*S*)	1/1	*R*	4	73
1	Valine (*S*)	2/1	*R*	21	71
1	Valine (*S*)	4/1	*R*	31	76
1	Valine (*R*)	4/1	*S*	35	78
1	Isoleucine (*S*)	2/1	*R*	26	67
1	Isoleucine (*R*)	2/1	*S*	24	68
1	Leucine (*S*)	2/1	*R*	11	64
1	Phenylalanine (*S*)	1/1		0	80
1	Phenylalanine (*S*)	2/1	*R*	6	70
2	Valine (*S*)	2/1	*R*	26	65
2	Alanine (*S*)	2/1	*R*	5	70
2	Phenylalanine (*S*)	2/1	*R*	7	68

a) Major enantiomer. b) The optical purities were determined on the basis of the specific rotations observed by reference to the values of the authentic samples.[1,2] c) The chemical yields were calculated on the basis of the amount of the amino acids used.

Table 2. Optical resolution of **1** and **2** with chiral amino acids in the presence of Fe^{3+}

Pyridoxal analog	Amino acid (confign.)	Fe^{3+} / Amino acid	**1** or **2** / Amino acid	Product		
				Confign.[a]	o.p./%[b]	c.y./%[c]
1	Valine (*S*)	1/1	2/1	*R*	20	87
1	Valine (*S*)	0.5/1	2/1	*R*	51	70
1	Valine (*S*)	0.5/1	4/1	*R*	70	76
1	Valine (*S*)	0.5/1	8/1	*R*	76	80
1	Valine (*R*)	0.5/1	2/1	*S*	54	68
1	Valine (*R*)	0.5/1	4/1	*S*	69	70
1	Leucine (*S*)	0.5/1	2/1	*R*	29	71
1	Leucine (*S*)	0.5/1	4/1	*R*	34	70
1	Leucine (*R*)	0.5/1	4/1	*S*	38	67
1	Isoleucine (*S*)	0.5/1	2/1	*R*	42	63
1	Isoleucine (*S*)	0.5/1	4/1	*R*	55	67
2	Valine (*S*)	0.5/1	2/1	*R*	50	72

a) Major enantiomer. b) The optical purities were determined on the basis of the specific rotations observed by reference to the values of the authentic samples.[1,2] c) The chemical yields were calculated on the basis of the amount of the amino acids used.

idinophanes. As the molar ratio of **1**/(*R*)-valine was increased, the apparent predominance of the intensity of the signals (a), (b) over (c), (d) was observed. These data sugested that (*R*)-valine coupled with (*S*)-**1** more preferentially than with (*R*)-**1**. In fact, the acidic hydrolysis of the Schiff base obtained through the reaction between (*R*)-valine and excess of racemic **1** and the subsequent removal of the unreacted **1** gave partially resolved **1** containing the (*S*)-enantiomer in excess. In the same way, employment of (*S*)-valine gave (*R*)-**1** in excess and employment of other chiral amino acids also resulted in the partial resolution of racemic **1**. The racemate of **2** was similarly resolved. The optical purities of the pyridinophanes isolated were determined by measuring their optical rotations. These results are shown in Table 1. The highest optical purities achieved by using valine indicated that the bulkiness of the α-substituents of the amino acids was important factor[12,13] dominating the optical purity of the products resolved. Throughout all runs, the efficiency of the resolution with amino acids seemed not so high.

In expectation of the enhancement of the optical purities of the resolution products, our attention was next directed towards addition of heavy metal ions to the reaction mixture for the Schiff base formation. It is known that some metal ions accelerate the formation of such Schiff bases, finally producing the chelate compounds of the Schiff bases.[14-17] Following preliminary experiments changing the metal ions employed, addition of iron(III) salt half equimolar to the amino acids served most effectively for the resolution of **1**. Furthermore, we found no racemization of the amino acid moiety in the Schiff base chelate complex (**13**) in the experiment using the system composed of **1**, chiral amino acid, and Fe^{3+} (4:1:0.5 in the molar ratio) under neutral conditions. On the basis of these preliminary results, the resolutions of racemic **1** and **2** were attempted in the presence of Fe^{3+} under neutral conditions, varying the kind and amount of the amino acid employed. The results are tabulated in Table 2. Again, the optical purity of the resolved pyridinophane (**1**) increased as the ratio of **1**/chiral amino acid increased, suggesting that this resolution is also ascribable to a kinetic asymmetric transformation.[18] The optical purities of **1** so obtained were almost twice obtained under similar conditions in the absence of Fe^{3+} (Table 1). In both cases, use of (*S*)-amino acids gave (*R*)-**1** in excess and *vice versa*. Use of a ratio larger than 4/1 for **1**/chiral amino acid resulted in no appreciable improvement in the optical purity of the product. Therefore, a combination of racemic pyridinophane–chiral valine–Fe^{3+} (4:1:0.5 in molar ratio) was regarded as the practical resolution system. Two treatments by this system were enough to give pure enantiomers of **1** and **2**.

The foregoing two types of resolution procedures using amino sugars and amino acids as the resolving agents differ from each other in several aspects. Concerning the resolution mechanisms, the former is based on the difference of the solubilities between the diastereomeric Schiff bases; whereas the later owes its specificity to the preferencial formation of one diastereomer; *i.e.*, to a difference in the reaction rate. In contrast to the readily available chiral amino acids, amino sugar derivatives are difficult to prepare. However, the efficiency of the optical resolution was much higher with the amino sugars than with amino acids.

Experimental

Solutions were evaporated under reduced pressure. Melting points are uncorrected. ^{1}H NMR spectra were recorded with a JEOL HA-100 spectrometer for amino sugar derivatives and with a JEOL JNM-FX 400 spectrometer for amino acid derivatives, using tetramethylsilane as the internal standard. Optical rotations were determined with a Perkin-Elmer Model 241 MC polarimeter. The racemic specimens of the pyridoxal-like pyridinophanes (**1** and **2**) were prepared according to our previous papers.[1,2]

3-Azido-3-deoxy-1,2:5,6-di-O-isopropylidene-β-D-idofuranose (7). Methanesulfonyl chloride (3.5 g) was added in portions at 0 °C to a solution of **8** (5.8 g) in dry pyridine (20 ml). The mixture was kept at the ambient temperature overnight, poured into ice-water, and extracted with chloroform. The extract was washed with 3% H_2SO_4, water, dried (Na_2SO_4) and evaporated to give **9** (6.4 g) as a yellow syrup: IR (film) 1185 cm^{-1}. To the solution of **9** in HMPA (35 ml) was added sodium azide (4.0 g). The mixture was heated at 100 °C with stirring for 11 h, cooled, diluted with ice-water (500 ml), and extracted with diethyl ether. The extract was washed with water, dried (Na_2SO_4) and evaporated to give a syrup (4.0 g). The syrup was chromatographed on silica gel with 5:1 (v/v) benzene–diethyl ether as the eluent to give **7** (3.3 g, 52% on the basis of **8**) as colorless crystals: mp 66—66.5 °C; $[\alpha]_D^{23}$ +74° (*c* 0.9, $CHCl_3$); IR(KBr) 2100 cm^{-1}. Found: C, 50.49; H, 6.76; N, 14.70%. Calcd for $C_{12}H_{19}O_5N_3$: C, 50.52; H, 6.71; N, 14.73%.

3-Amino-3-deoxy-1,2:5,6-di-O-isopropylidene-β-D-idofuranose (6). A solution of **7** (400 mg) in ethanol (20 ml) was stirred with Raney Ni (W-IV) in hydrogen atmosphere for 2 h. After filtration, the filtrate was evaporated to give crystalline **6** which was recrystallized from cyclohexane: yield 360 mg (99%); mp 98—98.5 °C; $[\alpha]_D^{22}$ +40° (*c* 0.26, $CHCl_3$); IR (KBr) 3380, 3330, and 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.24 (2H, s, NH_2), 3.35 (1H, d, $J_{3,4}$=4.0 Hz, H-3), and 5.93 (1H, d, $J_{1,2}$=3.5 Hz, H-1). Found: C, 55.68; H, 8.18; N, 5.24%. Calcd for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40%.

Preparation of Schiff Base Mixture (10) and Isolation of Less Soluble Diastereomer (10a). A solution of racemic **1** (100 mg) and **6** (100 mg) in benzene (10 ml) was placed in an open flask and heated for 1 h under gentle boiling. Evaporation of the residual solvent gave **10** as yellow powder: ^{1}H NMR ($CDCl_3$) δ=6.16 (0.5H, d, $J_{1',2'}$=4.0 Hz, H-1'), and 6.18 (0.5H, d, $J_{1',2'}$=4.0 Hz, H-1'). This powder was dissolved in a hot mixture of benzene (10 ml) and cyclohexane (6 ml) and then cooled, giving yellow crystals (78 mg): mp 139—140 °C. The crystals were recrystallized from a mixture of benzene (3.5 ml) and cyclohexane (3.5 ml) to give **10a**: yield 60 mg (65% on the basis of half of **1** used); mp 149—150 °C; $[\alpha]_D^{25}$ +236° (*c* 0.064, $CHCl_3$); IR (KBr) 3470 and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.16 (1H, d, $J_{1',2'}$= 4.0 Hz, H-1'), the doublet at 6.18 completely disappeared, 8.01 (1H, s, H-6 of the pyridine ring), 8.79 (1H, s, -CH= N-), and signals due to the solvent: 1.42 (6H, s, cyclohexane), and 7.32 (4H, s, benzene). Found: C, 62.31; H, 7.50; N, 4.17; S, 10.23%. Calcd for $C_{25}H_{36}O_6N_2S_2 \cdot 2/3\ C_6H_6 \cdot 1/2\ C_6H_{12}$: C, 62.11; H, 7.49; N, 4.53; S, 10.36%.

Acidic Hydrolysis of 10a to (R)-*1.* The Schiff base **10a** (400 mg) was dissolved in hot 1,4-dioxane (40 ml) and cool-

ed. After addition of 1 M (1 M=1 mol dm^{-3}) HCl (10 ml), the mixture was kept at room temperature for 40 min, diluted with water (250 ml), and extracted with ethyl acetate (300 ml). The extract was washed with aq $NaHCO_3$ and water successively, dried (Na_2SO_4), and evaporated to give (*R*)-**1** as a syrup, which was chromatographed on silica gel with 6:1 (v/v) benzene–diethyl ether as the eluent: yield 169 mg (92%); $[\alpha]_D^{17}$ +347° (*c* 1.05, $CHCl_3$) (lit[1]) for the antipode $[\alpha]_D^{24}$ −366°); IR (film) 3100 and 1660 cm^{-1}. Found: C, 55.64; H, 5.92; N, 4.86; S, 22.30%. Calcd for $C_{13}H_{17}O_2NS_2$: C, 55.09; H, 6.05; N, 4.94, S, 22.63%.

^1H NMR Measurement of the Schiff Bases Derived from **1** *and* (R)-*Valine.* A methanol solution (5 ml) of **1** (20.4 mg) and (*R*)-valine (4.1 mg) was stirred at room temperature overnight and evaporated. The resulting residue was dissolved in C_6D_6 (1 ml) and the NMR spectrum of the solution was recorded at 400 MHz.

Attempt for the Resolution of **1** *and* **2** *with Amino Acids in the Absence of Fe^{3+}.* A typical procedure for the resolution of **1** is exemplified in the following. A methanol solution (100 ml) containing (*S*)-valine (59 mg) and **1** (283 mg) was stirred at room temperature overnight. The methanol was evaporated and the residue was washed with 1:1 (v/v) benzene–hexane to remove the unreacted **1**, which was recycled. After addition of ethyl acetate (200 ml), the mixture was adjusted to pH 1 with 1 M HCl. The ethyl acetate solution was washed with water, dried ($MgSO_4$), and evaporated to give a yellow syrup, which was chromatographed on silica gel with 5:1 (v/v) benzene–diethyl ether as the eluent to give (*R*)-rich **1**: yield 100 mg (71% on the basis of valine); $[\alpha]_D^{23}$ +76° (*c* 0.16, $CHCl_3$); optical purity 21%.

Resolution of **1** *and* **2** *with Amino Acids in the Presence of Fe^{3+}.* A typical procedure is exemplified in the following. To a stirred solution of (*S*)-valine (47 mg), 0.1 M methanolic sodium methoxide (4 ml), and **1** (453 mg) in methanol (200 ml) was added dropwise a solution of $Fe(ClO_4)_3 \cdot 8H_2O$ (100 mg) in methanol (50 ml). The mixture was stirred at room temperature overnight. The pH value of the media was around 7 during the reaction. Methanol was evaporated and the resulting residue was washed with chloroform. Ethyl acetate was added to the residue and the mixture was adjusted to pH 1 with 1 M HCl. The ethyl acetate solution was washed with water, dried ($MgSO_4$), and evaporated to dryness. The resulting residue was chromatographed on silica gel with 5:1 (v/v) benzene–diethyl ether as the eluent to give (*R*)-rich **1**: yield 86 mg (76% on the basis of valine), $[\alpha]_D^{24}$ +256° (*c* 0.12, $CHCl_3$); optical purity 70%. The aqueous layer underwent ion-exchange chromatography as described in the previous paper[3] to give 38 mg of valine; $[\alpha]_D^{23}$ +27.6° (*c* 0.90, 6 M HCl) (authentic (*S*)-valine $[\alpha]_D^{23}$ +28.8° (*c* 1.10, 6 M HCl)). The 70% optically pure (*R*)-**1** (80 mg), (*S*)-valine (28 mg), 0.1 M methanolic sodium methoxide (2.4 ml), and $Fe(ClO_4)_3 \cdot 8H_2O$ (60 mg) were treated again in methanol (200 ml). After a similar work up to the first resolution, almost pure (*R*)-**1** was obtained: yield 46 mg (68% on the basis of valine); $[\alpha]_D^{23}$ +360° (*c* 0.13, $CHCl_3$).

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