Optical Resolution by Preferential Crystallization of (1*RS*,3*RS*)-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid

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The racemic structure of (1*RS*,3*RS*)-1,2,3,4-tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic acid [(1*RS*,3*RS*)-1] was examined based on the melting point, solubility, and IR spectrum, with the aim of optical resolution by preferential crystallization. (1*RS*,3*RS*)-1 was indicated from these results to exist as a conglomerate. The successive optical resolution by preferential crystallization of (1*RS*,3*RS*)-1 yielded (1*S*,3*S*)- and (1*R*,3*R*)-1 with optical purities of 85—95% at 66—81% degrees of resolution, which were fully purified by recrystallization.

Key words 1,2,3,4-tetrahydroisoquinoline; conglomerate; optical resolution; preferential crystallization

(1*S*,3*S*)-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic acid [(1*S*,3*S*)-**1**] is the alkaloid from seeds of the genus *Mucuna* (Leguminosae).[1] (1*S*,3*S*)-**1** is a physiologically important compound and, for example, is potent in free radical-scavenging activity against hydroxyl and superoxide anion radicals.[2] In addition, (1*S*,3*S*)- and (1*R*,3*R*)-**1** are useful as chiral reagents in asymmetric syntheses; for example, (8*S*,13a*R*)-8-methyl-2,3,10,11-tetramethoxyberbine is synthesized from (*S*)-2-amino-3-(3,4-dihydroxyphenyl)propanoic acid [(*S*)-**2**; L-3,4-dihydroxyphenylalanine (L-DOPA)] *via* the (1*S*,3*S*)-**1** intermediate.[3] (1*S*,3*S*)-**1** can be synthesized by condensation of (*S*)-**2** with acetaldehyde in dilute aqueous mineral acid *in vitro*. The condensation affords compound **1** as a mixture of two diastereoisomers, the major product (1*S*,3*S*)-**1** (*cis*-form) and the minor product (1*R*,3*S*)-**1** (*trans*-form), because of the generation of a new chiral center at the C-1 position of the 1,2,3,4-tetrahydroisoquinoline ring.[4] From the mixture of the diastereoisomers, (1*R*,3*S*)-**1** was removed by recrystallization from dilute hydrochloric acid to afford (1*S*,3*S*)-**1** as the single diastereoisomer without formation of the hydrochloride, as described in Experimental. Although (1*R*,3*R*)- and (1*RS*,3*RS*)-**1** can be also synthesized starting from (*R*)- and (*RS*)-**2**, respectively, in a manner similar to (1*S*,3*S*)-**1**,[5] (*R*)-**2** is not commercially available. Therefore we attempted to obtain both (1*S*,3*S*)- and (1*R*,3*R*)-**1** by optical resolution by preferential crystallization of (1*RS*,3*RS*)-**1** (Chart 1).

Optical resolution by preferential crystallization, which has been successfully employed to obtain enantiomers from racemates, is said to be a simple and useful method for large-scale chiral separation and is achieved by providing a small amount of one enantiomer as seed crystals in a racemic supersaturated solution.[6—9] Racemates exist in the forms of racemic compounds, racemic solid solutions, and conglomerates. However, only conglomerates, which are defined as mechanical mixtures of crystals of both enantiomers, can be optically resolved by preferential crystallization. Therefore we first examined the racemic structure of (1*RS*,3*RS*)-**1**.

The racemic structure was examined by comparing the melting point, solubility, and IR spectrum of the racemate with those of the enantiomer.[6,7] Although (1*RS*,3*RS*)- and (1*S*,3*S*)-**1** were decomposed by heating, (1*RS*,3*RS*)-**1** was decomposed at a lower temperature during heating than was (1*S*,3*S*)-**1**. The IR spectrum of (1*RS*,3*RS*)-**1** was identical to that of (1*S*,3*S*)-**1**. In addition, (1*RS*,3*RS*)-**1** was more soluble than (1*S*,3*S*)-**1**: the solubility of (1*RS*,3*RS*)-**1** at 10 °C was 1.396 g (100 ml of 0.1 mol/l HCl)$^{-1}$; and the solubility of (1*S*,3*S*)-**1** at 10 °C was 0.799 g (100 ml of 0.1 mol/l HCl)$^{-1}$. Racemates that exist as a conglomerates are known to have such characteristics.[6,7] In addition, the ternary solubility diagram also showed that (1*RS*,3*RS*)-**1** is expected to be a conglomerate (Fig. 1). The above results suggest that (1*RS*,3*RS*)-**1** exists as a conglomerate.[6,7]

(1*RS*,3*RS*)-**1** was optically resolved by preferential crystallization in 0.1 mol/l hydrochloric acid at 10 °C. To optimize the conditions, the optical resolution was conducted by stirring solutions of (1*RS*,3*RS*)-**1** in 50 ml of 0.1 mol/l hydrochloric acid at 140—170% supersaturation for 30—90 min; (1*S*,3*S*)-**1** (0.100 g) was employed as seed crystals. The results are shown in Figs. 2 and 3. The yield of enantiomer [*YE* (g)], degree of resolution [*DR* (%)], and amount of crystallization [$AC_{(1S,3S)}$ and $AC_{(1R,3R)}$ (g)] were calculated from

$$YE\,(\mathrm{g}) = [\mathrm{yield}\,(\mathrm{g}) \times OP\,(\%)/100] - 0.100$$

$$DR\,(\%) = YE\,(\mathrm{g}) \times 100/\{(1/2)[\mathrm{amount\ of}\ (1RS,3RS)\text{-}\mathbf{1}\,(\mathrm{g}) - 0.698]\}$$

$$AC_{(1R,3R)}\,(\mathrm{g}) = (1/2)[\mathrm{yield}\,(\mathrm{g}) - YE\,(\mathrm{g}) - 0.100]$$

$$AC_{(1S,3S)}\,(\mathrm{g}) = YE\,(\mathrm{g}) + AC_{(1R,3R)}\,(\mathrm{g})$$

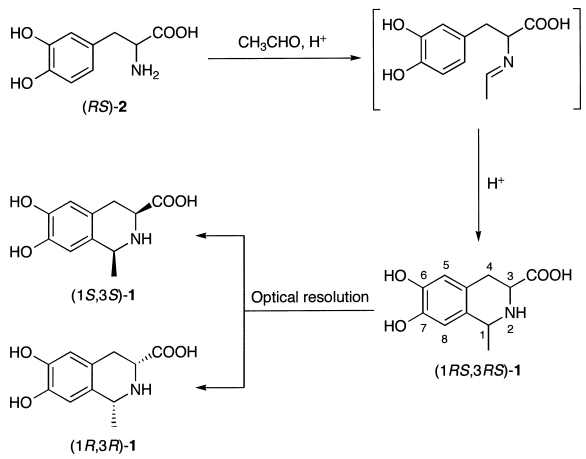

Chart 1. Synthetic Route to Optically Active *cis*-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid (*cis*-**1**)

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where the solubility of (1*RS*,3*RS*)-**1** was 0.698 g in 50 ml of 0.1 mol/l hydrochloric acid at 10 °C, the yield is the sum of the amounts of the crystallized **1** and seed crystals, and the optical purity [*OP* (%)] of the obtained (1*S*,3*S*)-**1** is calculated on the basis of the specific rotation ($[\alpha]_D^{20}$ −157° (*c*=1, 1 mol/l HCl)) of (1*S*,3*S*)-**1**, which was synthesized from (*S*)-**2**; (1*S*,3*S*)-**1**, $[\alpha]_D$ −151.5° (*c*=1, 1 mol/l HCl)[4]; (1*R*,3*R*)-**1**, $[\alpha]_D$ +157.4° (*c*=1, 1 mol/l HCl).[5] The degree of resolution [*DR* (%)] is defined as the yield (%) of the seeded enantiomer, based on half of the supersaturating portion of a racemate, and indicates the efficiency of optical resolution; half of the supersaturating portion of a racemate means the theoretical yield (g) of the seeded enantiomer.

When the 140—155% supersaturated solutions were employed (Fig. 2), (1*S*,3*S*)-**1** with optical purities of about 90% were obtained with 49—63% degrees of resolution. When the solutions with 160% and 170% supersaturation were employed (Fig. 2), the optical resolutions gave (1*S*,3*S*)-**1** with optical purities of 71% and 37%, respectively, because of rapid crystallization of the unseeded (1*R*,3*R*)-**1**. From these results, the optical resolution of the 155% supersaturated solution was determined at resolution times of 30—90 min (Fig. 3). Rapid crystallization of the unseeded (1*R*,3*R*)-**1** was not observed for the first 70 min, but (1*R*,3*R*)-**1** began to crystallize rapidly at 80 min. Therefore (1*S*,3*S*)-**1** with optical purity of 85% was obtained in the highest degree of resolution (70%) at resolution time of 70 min. Based on these results, successive optical resolution was attempted by stirring the 155% supersaturated solution, as the initial solution, for 70 min (Table 1). The degrees of resolution [*DR* (%)] of (1*S*,3*S*)- and (1*R*,3*R*)-**1** obtained were calculated from

$$DR\,(\%) = YE\,(\text{g}) \times 100 / [\text{operation amount of } (1S,3S)\text{- or } (1R,3R)\text{-}\mathbf{1}\,(\text{g}) - 0.349]$$

where the operation amount is the amount of (1*S*,3*S*)- and (1*R*,3*R*)-**1** in the solution used in the optical resolution and those in runs 2—4 in Table 1 were calculated based on the yields and optical purities of (1*S*,3*S*)- and (1*R*,3*R*)-**1** obtained

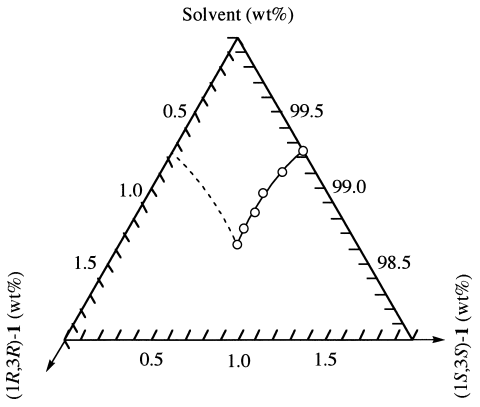

Fig. 1. Solubility Ternary Phase Diagram of *cis*-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid (*cis*-**1**)

Conditions: temperature, 10 °C; solvent, 0.1 mol/l hydrochloric acid.

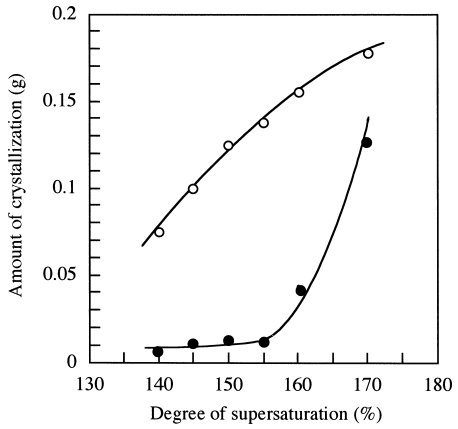

Fig. 2. Relationship between the Amount of Crystallization and Degree of Supersaturation in the Optical Resolution of (1*RS*,3*RS*)-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid [(1*RS*,3*RS*)-**1**]

Conditions: (1*RS*,3*RS*)-**1**, 0.977—1.187 g (140—170% supersaturation); seed crystals, 0.100 g of (1*S*,3*S*)-**1**; solvent, 50 ml of 0.1 mol/l hydrochloric acid; resolution time, 60 min; temperature, 10 °C. Amount of crystallization: ○, (1*S*,3*S*)-**1**; ●, (1*R*,3*R*)-**1**.

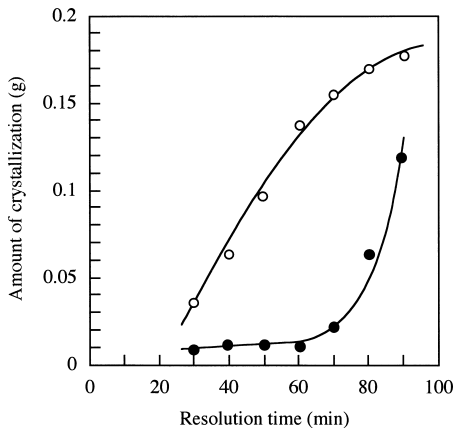

Fig. 3. Relationship between the Amount of Crystallization and Resolution Time in the Optical Resolution of (1*RS*,3*RS*)-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid [(1*RS*,3*RS*)-**1**]

Conditions: (1*RS*,3*RS*)-**1**, 1.082 g (155% supersaturation); seed crystals, 0.100 g of (1*S*,3*S*)-**1**; solvent, 50 ml of 0.1 mol/l hydrochloric acid; resolution time, 30—90 min; temperature, 10 °C. Amount of crystallization: ○, (1*S*,3*S*)-**1**; ●, (1*R*,3*R*)-**1**.

Table 1. Successive Optical Resolution by Preferential Crystallization of (1*RS*,3*RS*)-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid[a]

Run	Amount of (1*RS*,3*RS*)-**1** added (g)	Operation amount (g)		Resolution time (min)	Yield[b] (g)	Optical purity (%)	*YE*[c] (g)	*DR*[d] (%)
		(1*S*,3*S*)-**1**	(1*R*,3*R*)-**1**					
1	1.082	0.541	0.541	70	(1*S*,3*S*)-(−) 0.276	84.7	0.134	70
2	0.176	0.474	0.608	80	(1*R*,3*R*)-(+) 0.320	92.4	0.196	76
3	0.220	0.572	0.510	60	(1*S*,3*S*)-(−) 0.285	87.0	0.148	66
4	0.186	0.498	0.584	80	(1*R*,3*R*)-(+) 0.307	94.9	0.191	81

a) Conditions: seed crystals of (1*S*,3*S*)- or (1*R*,3*R*)-**1**, 0.100 g; solvent, 50 ml of 0.1 mol/l hydrochloric acid; temperature, 10 °C. *b*) The yield is the sum of the amounts of crystallized **1** and seed crystals. *c*) *YE*, yield of enantiomer. *d*) *DR*, degree of resolution.

in runs 1—3, respectively. Half of the solubility of (1*RS*,3*RS*)-**1** is 0.349 g in 50 ml of 0.1 mol/l hydrochloric acid at 10 °C.

The optical resolution afforded (1*S*,3*S*)- and (1*R*,3*R*)-**1** with optical purities of 85—95% at 66—81% degrees of resolution. The (1*S*,3*S*)- and (1*R*,3*R*)-**1** obtained were recrystallized from 0.1 mol/l hydrochloric acid to afford the optically pure **1** enantiomers.

Experimental

General Specific rotations were measured at 589 nm and 20 °C with a Horiba Seisakusho SEPA-300 autopolarimeter equipped with a quartz cell with a 5.00-cm path length. IR spectra were obtained in the range of 4000—400 cm^{-1} with a Perkin-Elmer Model 1600 FT-IR spectrometer using the KBr disk method. ^{1}H- and ^{13}C-NMR spectra were recorded on a JNM-FX270 FT NMR system in a deuterium oxide solution of deuterium chroride (DCl) with sodium 3-(trimethylsilyl)propane-1-sulfonate (DSS) as an internal standard. Chemical shifts are reported in δ units downfield from DSS. Melting points were measured with a Yanaco MP-500 D micro melting point apparatus.

(1*RS*,3*RS*)-, (1*S*,3*S*)-, and (1*R*,3*R*)-1,2,3,4-Tetrahydro-6,7-dihydroxy-1-methyl-3-isoquinolinecarboxylic Acid [(1*RS*,3*RS*)-, (1*S*,3*S*)-, and (1*R*,3*R*)-1] To the solution of (*RS*)-**2** (19.7 g, 0.100 mol) in 0.1 mol/l hydrochloric acid (1000 ml) acetaldehyde [49 g (about 90%), 1 mol] was added. After allowing to stand overnight at room temperature, the solution was evaporated to dryness *in vacuo* at 60 °C. A solution of the residue in 300 ml of methanol was adjusted with triethylamine to pH 7 to precipitate (1*RS*,3*RS*)-**1**. After suspending in 300 ml of boiling water for 1 h, (1*RS*,3*RS*)-**1** was collected quickly by filtration and dried.

(1*RS*,3*RS*)-**1**: Yield, 16.5 g (74.0%); mp 270—275 °C (decomp.). IR (KBr) cm^{-1}: 3103, 1631, 1549, 1524, 1441, 1401, 1313, 852, 808, 624. ^{1}H-NMR (270 MHz, 0.1 mol/l DCl, DSS) δ: 6.82 (1H, s, arom. H), 6.77 (1H, s, arom. H), 4.59 (1H, q, J=6.8 Hz, 1-CH), 4.35 (1H, dd, J=5.3, 12.0 Hz, 3-CH), 3.32 (1H, dd, J=5.4, 16.2 Hz, 4-CHH), 3.16 (1H, dd, J=12.1, 16.0 Hz, 4-CHH), 1.70 (3H, d, J=6.8 Hz, $-CH_3$). ^{13}C-NMR (67.5 MHz, 0.1 mol/l DCl, DSS) δ=171.7 (–COOH), 144.6 (arom. C), 144.1 (arom. C), 125.1 (arom. C), 123.0 (arom. C), 116.1 (arom. C), 113.3 (arom. C), 55.4 (1-C), 53.0 (3-C), 28.7 (4-C), 18.6 (-CH_3). *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 58.97; H, 5.70; N, 6.30.

(1*S*,3*S*)-**1** was synthesized by reaction of (*S*)-**2** (1.97 g, 10.0 mmol) with acetaldehyde (4.89 g, 0.100 mol), in a similar manner to that for (1*RS*,3*RS*)-**1**; $[\alpha]_D^{20}$ −139° (c=1.00, 0.1 mol/l HCl). After vigorous stirring, a suspension of the crude (1*S*,3*S*)-**1** (1.82 g) in 15 ml of 0.1 mol/l hydrochloric acid for 1 h at 80 °C and then at 10 °C for 3 h, the purified (1*S*,3*S*)-**1** was collected by filtration, washed with a small amount of water, and dried.

(1*S*,3*S*)-**1**: Yield, 1.55 g (69.5%); mp 288—291 °C (decomp.) [mp 280—281 °C (decomp.)][4]; $[\alpha]_D^{20}$ −157° (c=1.00, 1 mol/l HCl) {$[\alpha]_D$ −151.5° (c=1, 1 mol/l HCl)}.[4] The IR, ^{1}H-, and ^{13}C-NMR spectra were virtually identical to those of (1*RS*,3*RS*)-**1**. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.03; H, 5.78; N, 6.27.

The crude (1*R*,3*R*)-**1** (2.20 g) was obtained from the mother liquors, after preferential crystallization of (1*S*,3*S*)-**1** by optical resolution using (1*S*,3*S*)-**1** as the seed crystals; $[\alpha]_D^{20}$ +17.5° (c=1.00, 1 mol/l HCl). After dissolving the crude (1*R*,3*R*)-**1** (2.14 g) in 140 ml of 0.1 mol/l hydrochloric acid at 80 °C, the solution was vigorously stirred for 5 h at 10 °C to precipitate enantiopure (1*R*,3*R*)-**1**.

(1*R*,3*R*)-**1**: Yield, 0.221 g; mp 289—292 °C (decomp.) [mp 285—287 °C (decomp.)][5]; $[\alpha]_D^{20}$ +157° (c=1.00, 1 mol/l HCl) {$[\alpha]_D$ +157.4° (c=1, 1 mol/l HCl)}.[5] The IR, ^{1}H-, and ^{13}C-NMR spectra were virtually identical to those of (1*RS*,3*RS*)-**1**. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.01; H, 5.83; N, 6.23.

Optical Resolution by Preferential Crystallization (1*RS*,3*RS*)-**1** (0.977—1.187 g) was dissolved in 50 ml of 0.1 mol/l hydrochloric acid at 40 °C to prepare 140—170% supersaturated solutions at 10 °C. The solutions were cooled to 10 °C over a period of 30 min and then seeded with 0.100 g of (1*S*,3*S*)-**1**. After stirring the mixture with a magnetic stirrer for 30—90 min at 10 °C, (1*S*,3*S*)-**1** was collected by filtration and dried.

(1*S*,3*S*)-**1** obtained from 140% supersaturated solution at 60 min: Yield 0.181 g; $[\alpha]_D^{20}$ −146° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 145% supersaturated solution at 60 min: Yield 0.211 g; $[\alpha]_D^{20}$ −139° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 150% supersaturated solution at 60 min: Yield 0.238 g; $[\alpha]_D^{20}$ −138° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 30 min: Yield 0.144 g; $[\alpha]_D^{20}$ −139° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 40 min: Yield 0.177 g; $[\alpha]_D^{20}$ −134° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 50 min: Yield 0.209 g; $[\alpha]_D^{20}$ −137° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 60 min: Yield 0.247 g; $[\alpha]_D^{20}$ −139° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 70 min: Yield 0.276 g; $[\alpha]_D^{20}$ −133° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 80 min: Yield 0.334 g; $[\alpha]_D^{20}$ −96.8° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 155% supersaturated solution at 90 min: Yield 0.396 g; $[\alpha]_D^{20}$ −62.6°(c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 160% supersaturated solution at 60 min: Yield 0.299 g; $[\alpha]_D^{20}$ −111° (c=1.00, 0.1 mol/l HCl). (1*S*,3*S*)-**1** obtained from 170% supersaturated solution at 60 min: Yield 0.404 g; $[\alpha]_D^{20}$ −58.4° (c=1.00, 0.1 mol/l HCl).

Successive Optical Resolution by Preferential Crystallization (1*RS*,3*RS*)-**1** (1.082 g) was dissolved in 50 ml of 0.1 mol/l hydrochloric acid at 40 °C to prepare a 155% supersaturated solution at 10 °C. The solution was cooled to 10 °C over a period of 30 min and then seeded with 0.100 g of (1*S*,3*S*)-**1**. After stirring the mixture with a magnetic stirrer for 70 min at 10 °C, (1*S*,3*S*)-**1** (0.276 g) was collected by filtration and dried (run 1 in Table 1). (1*RS*,3*RS*)-**1** (0.176 g) was dissolved in the filtrate at 40 °C and the resulting solution was cooled to 10 °C. After adding (1*R*,3*R*)-**1** (0.100 g) as seed crystals to the solution, followed by stirring the mixture for 80 min at 10 °C, (1*R*,3*R*)-**1** (0.320 g) was collected by filtration and dried (run 2 in Table 1). Optical resolution was carried out at 10 °C by adding further (1*RS*,3*RS*)-**1** to the filtrates in a manner similar to that described above; the detailed conditions are shown in runs 3 and 4 in Table 1.

Solubility and Ternary Phase Diagram After vigorously stirring (1*RS*,3*RS*)-**1** (1.000 g) or (1*S*,3*S*)-**1** (1.000 g) in 40 ml of 0.1 mol/l hydrochloric acid for 1 h at 60 °C, followed by stirring for 10 h at 10 °C, the precipitated (1*RS*,3*RS*)- or (1*S*,3*S*)-**1** was rapidly collected by filtration and thoroughly dried. The solubility at 10 °C was calculated on the basis of the weight of the precipitated (1*RS*,3*RS*)- or (2*S*,3*S*)-**1**. Solubility of the (1*RS*,3*RS*)-**1** at 10 °C: 1.396 g (100 ml of 0.1 mol/l HCl)$^{-1}$. Solubility of (1*S*,3*S*)-**1** at 10 °C: 0.799 g (100 ml of 0.1 mol/l HCl)$^{-1}$.

Preparing a ternary solubility diagram, the solubilities of mixtures of (1*RS*,3*RS*)- and (1*S*,3*S*)-**1** were measured at 10 °C similar to the method described above. The solid **1** was filtered off and thoroughly dried and the specific rotation was measured. The amounts of (1*R*,3*R*)- and (1*S*,3*S*)-**1** in the solution were calculated based on the solubility of **1** and the specific rotation of the solid **1**.

Acknowledgments This research was financially supported by a "High-Tech Research Center" Project for Private Universities: matching fund subsidy from the Ministry of Education, Culture, Sports, Science and Technology, Japan, 2002—2006.

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