Preparation of Optically Active 2-Thiazolidinecarboxylic Acid by Asymmetric Transformation

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Cysteamine was condensed with glyoxylic acid monohydrate in a mixture of acetic acid and ethanol in the presence of (2*R*,3*R*)- or (2*S*,3*S*)-tartaric acid [(*R*)- or (*S*)-TA], as the resolving agent, to give the salt of (−)-2-thiazolidinecarboxylic acid [(−)-2-THC] with (*R*)-TA or the salt of (+)-2-THC with (*S*)-TA. Treatment of these salts with triethylamine in methanol afforded (−)- and (+)-2-THC. The (−)- and (+)- 2-THC obtained were determined to be enantiopure forms by comparing their powder X-ray diffraction patterns with that of (*RS*)-2-THC. The absolute configurations of (−)- and (+)-2-THC were estimated based on molar rotations of (2*R*,4*R*)- and (2*S*,4*R*)-2,4-thiazolidinedicarboxylic acids, (*R*)-4-thiazolidinecarboxylic acid, and (−)- and (+)-2-THC. (−)-2-THC was determined to have the (*R*)-configuration, and (+)-2-THC to have the (*S*)-configuration.

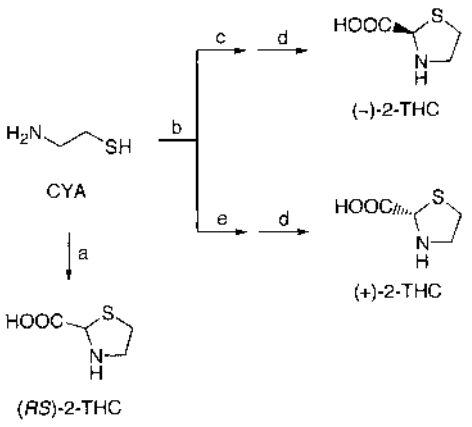
Key words 2-thiazolidinecarboxylic acid; asymmetric transformation; absolute configuration; tartaric acid; powder X-ray diffraction pattern

Some thiazolidine derivatives may be of biological significance. For example, 2-thiazolidinecarboxylic acid (2-THC) has been reported to be a substrate for hog kidney D-amino acid oxidase.[1] (*RS*)-2-THC is obtained by condensation of cysteamine (CYA) with glyoxylic acid (GLA).[2—4] Although (*RS*)-2-THC ethyl ester has been optically resolved using (2*R*,3*R*)- and (2*S*,3*S*)-tartaric acid [(*R*)- and (*S*)-TA] as the resolving agent to afford both enantiomers,[5] free optically active 2-THC has not yet been obtained because of the rapid racemization which occurs during hydrolysis of the optically active esters.[2,5] In addition, thiazolidine derivatives with a chiral center at the C-2 position are known to be prone to racemization or epimerization at the C-2 position by interconversion between the enantiomers or diastereoisomers *via* a ring opening intermediate.[2,6—9] These data suggested that optically active 2-THC readily undergoes racemization in solution. The asymmetric transformation of DL-α-amino acids has been carried out in carboxylic acids, such as acetic acid, under heterogeneous conditions by combination of selective crystallization of a less soluble diastereoisomeric salt with epimerization of a more soluble salt in solution.[10,11] Therefore, we attempted to prepare optically active 2-THC *via* asymmetric transformation by taking advantage of its ease of racemization in solution.

First, we attempted to synthesize (*RS*)-2-THC under conditions similar to those of asymmetric transformation. (*RS*)-2-THC was obtained in a yield of 88.5% by condensation of CYA with GLA monohydrate (GLA·H_2O) in a mixture of acetic acid and ethanol at 30 °C under heterogeneous conditions (Chart 1). A mixture of acetic acid and ethanol in a volume ratio of 1 : 1.5 was employed as the solvent because (*RS*)-2-THC completely dissolved in acetic acid even at 30 °C. The formation of (*RS*)-2-THC was determined by the ^{1}H-NMR and ^{13}C-NMR spectra and elemental analyses.

Next, the asymmetric transformation was attempted to prepare optically active 2-THC. In general, α-amino acids do not form salts with optically active TA as the resolving agent. However, cyclic α-amino acids such as 4-thiazolidinecarboxylic acid[12] (4-THC) and proline[13,14] were reported to be optically resolved by separating diastereoisomeric salts with optically active TA. 2-THC, which is a cyclic α-amino acid and regioisomer of 4-THC, also may undergo salt formation with TA. Therefore, we employed optically active TA as the resolving agent for asymmetric transformation of (*RS*)-2-THC. In addition, carbonyl compounds are employed as epimerization catalysts in asymmetric transformation of DL-α-amino acids.[14,15] However, such epimerization catalysts were not employed in this asymmetric transformation because optically active 2-THC seemed to be rapidly racemized even in the absence of the catalyst.

CYA was reacted with equimolar GLA·H_2O in the presence of (*R*)- or (*S*)-TA for 2 h at 80 °C because asymmetric transformation of DL-α-amino acids is usually carried out at relatively high temperature.[14,15] The reaction gave a salt of (−)-2-THC with (*R*)-TA [(−)-2-THC·(*R*)-TA salt] and (+)-2-THC·(*S*)-TA salt in yields of 64 and 60%, respectively (Chart 1); (−)-2-THC·(*R*)-TA salt, $[\alpha]_D^{20}$ −42.2 (c=0.100, pyridine); (+)-2-THC·(*S*)-TA salt, $[\alpha]_D^{20}$ +42.2 (c=0.100, pyridine). The specific rotations were rapidly measured in pyridine because the specific rotations underwent no changes after standing the pyridine solutions for at least 1 h at 20 °C; the specific rotations of the salts changed in water and



Reagents and Conditions: (a) GLA·H_2O, mixture of acetic acid and ethanol, 30°C, 3 h; (b) GLA·H_2O, mixture of acetic acid and ethanol, 30–90°C, 2 h; (c) (*R*)-TA; (d) triethylamine, methanol; (e) (*S*)-TA.

Chart 1. Synthetic Routes to Optically Active 2-THC

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DMSO and the absolute values decreased as time passed. The salts obtained were demonstrated by ^{1}H-NMR spectra and elemental analyses to be composed of equimolar amounts of 2-THC and TA. (−)-2-THC and (+)-2-THC were obtained from the salts by treatment of methanol suspensions with triethylamine in yields of 39 and 36%, respectively, based on the amount of the starting CYA; (−)-2-THC, $[\alpha]_D^{20}$ −110 (c=0.100, pyridine); (+)-2-THC, $[\alpha]_D^{20}$ +110 (c=0.100, pyridine). Although the (−)- and (+)-2-THC obtained here show specific rotations whose absolute values were large, this does not prove them to be enantiopure. Therefore, the optical purities of (−)- and (+)-2-THC were examined by powder X-ray diffraction patterns.

Although (*RS*)-, (−)-, and (+)-2-THC were decomposed by heating, (*RS*)-2-THC had a higher decomposition point than those of (−)- and (+)-2-THC. In addition, the IR spectrum of (*RS*)-2-THC was different from those of (−)- and (+)-2-THC. Therefore, (*RS*)-2-THC was determined to have formed a racemic compound.[16] Although racemates exist in the form of racemic compounds, racemic solid solutions, and conglomerates, racemates and the corresponding enantiomers give distinctive powder X-ray diffraction patterns only when they form racemic compounds.[16] The powder X-ray diffraction pattern obtained for (−)-2-THC was identical to that for (+)-2-THC. On the other hand, the pattern of (*RS*)-2-THC was distinct from those of (−)- and (+)-2-THC. The powder X-ray diffraction pattern data of (−)-, (+)-, and (*RS*)-2-THC are given in the Experimental section. X-Ray diffraction patterns of a mixture of 95 mass% (−)-2-THC and 5% (*RS*)-2-THC and the present (−)-2-THC were compared at 2θ *ca.* 20.5° with the aid of the peak fitting. The mixed sample gave 3 peaks from (−)-2-THC [d=432 pm (relative intensity=100), 434 pm (77.4), 438 pm (13.2)] and 1 peak from (*RS*)-2-THC [426 pm (8.4)], while the present (−)-2-THC sample gave 4 peaks [432 pm (100), 434 pm (74.8), 438 pm (16.9), 424 pm (1.4)]. For the latter set of peaks, the first three peaks came from (−)-2-THC because they did not appear in the diffraction pattern of (*RS*)-2-THC, but the last one may come from (−)-2-THC and/or (*RS*)-2-THC. Even if it was assigned wholely to (*RS*)-2-THC, the mass percentage of (*RS*)-2-THC in the present mixture would be 0.83% based on the intensity ratios; thus the optical purity of the present (−)-2-THC was estimated to be over 99%. Therefore, the (−)- and (+)-2-THC samples obtained here were determined on the basis of the above results and specific rotations to be enantiopure forms.

The absolute configurations of compounds containing several chiral centers can be assigned based on the sum of the experimental molar rotations of suitable fragments.[17] (*R*)-2-THC and (*R*)-4-THC[12] can be regarded as fragments of (2*R*,4*R*)-2,4-thiazolidinedicarboxylic acid[9] [(2*R*,4*R*)-TDA] and (*S*)-2-THC and (*R*)-4-THC as those of (2*S*,4*R*)-TDA. The sum of the molar rotations of (−)-2-THC ($[M]_D^{20}$ −146 (c=0.100, pyridine)) and (*R*)-4-THC ($[M]_D^{20}$ −185 (c=0.100, pyridine)) was calculated to be −331 in good agreement with the experimental molar rotation ($[M]_D^{20}$ −335 (c=0.100, pyridine)) of (2*R*,4*R*)-TDA. In addition, the molar rotation of (2*S*,4*R*)-TDA was calculated on the basis of those of (+)-2-THC and (*R*)-4-THC to be −39 and agreed with the experimental data ($[M]_D^{20}$ −31.4 (c=0.100, pyridine)). Therefore, (−)-2-THC was determined to have the (*R*)-configuration and (+)-2-THC to have the (*S*)-configuration.

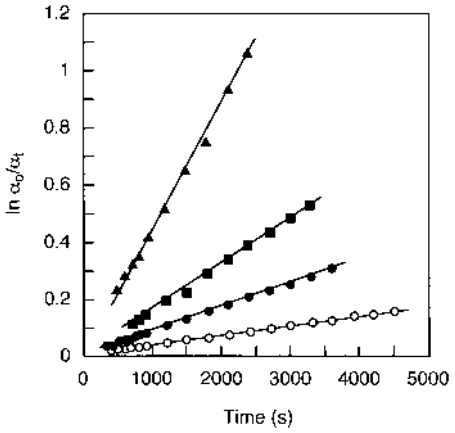

Fig. 1. Racemization of Optically Active 2-THC

Conditions: (*R*)-2-THC, 0.050 g; acetic acid, 10 cm^3. Temperature: ○, 20 °C; ●, 25 °C; ■, 30 °C; ▲, 35 °C. α_0: Optical rotation extrapolated to time zero. α_t: Optical rotation at time t.

Although the above results indicated that enantiopure (*R*)- and (*S*)-2-THC were obtained by asymmetric transformation using (*R*)- and (*S*)-TA as the resolving agent, respectively, the reaction at 80 °C did not give satisfactory yields. Therefore, in order to examine the possibility of asymmetric transformation at temperatures lower than 80 °C, the racemization rate of (*R*)-2-THC was measured in acetic acid at 20—35 °C (Fig. 1).

The racemization of (*R*)-2-THC obeyed first-order kinetics, as shown in Fig. 1. The rate constants (k_R (s^{-1})) at 20, 25, 30 and 35 °C were calculated to be 3.36×10^{-5}, 8.45×10^{-5}, 1.59×10^{-4} and 4.36×10^{-4} s^{-1}, respectively; the measurement of racemization rate in water at 20 °C yielded the k_R value of 1.24×10^{-4} s^{-1}. The apparent activation energy was calculated from the plot of ln k_R *vs.* $1/T$ to be 125 kJ mol^{-1} in acetic acid and the frequency factor to be 6.46×10^{17} s^{-1}; the correlation coefficient was 0.996. When the optically active substance gives the k_R value of over 1×10^{-3} s^{-1}, the asymmetric transformation of its racemate is successfully achieved.[18] The k_R values at 50 and 60 °C were estimated by extrapolation of the linear ln k_R *vs.* $1/T$ plot at 20—35 °C to be 3.9×10^{-3} and 1.6×10^{-2} s^{-1}, respectively. The above result of racemization suggested the possibility of asymmetric transformation at temperatures lower than 80 °C. Therefore, CYA was reacted with GLA·H_2O in the presence of equimolar (*R*)-TA for 2 h at 30—70 °C in a mixture of acetic acid and ethanol; asymmetric transformation was also carried out at 90 °C. The results are given in Table 1.

When the reaction was carried out at 30—60 °C, (*R*)-2-THC·(*R*)-TA salt was obtained in an approximately constant yield (over 80%). The absolute value of specific rotation of the salt increased with increasing reaction temperature. The (*R*)-2-THC·(*R*)-TA salt obtained by reaction at 60 °C showed specific rotation $[\alpha]_D^{20}$ of −42.2 (c=0.100, pyridine); yield 83%. When the reaction was carried out at 70—90 °C, the yield of (*R*)-2-THC·(*R*)-TA salt was rapidly reduced with increasing reaction temperature though the salt showed the constant specific rotation $[\alpha]_D^{20}$ of −42 (c=0.100, pyridine). The (*R*)-2-THC·(*R*)-TA salt obtained at 60 °C was treated with triethylamine in methanol to give enantiopure (*R*)-2-THC in a yield of 52%, based on the amount of the starting

Table 1. Preparation of Optically Active 2-THC by Asymmetric Transformation[a)]

Temperature (°C)	2-THC·TA salt			2-THC		
	Configuration[b)]	Yield (g) [%[c)]]	Specific rotation[d)]	Configuration	Yield (g) [%[c)]]	Specific rotation[d)]
30[e)]	(*R*)·(*R*)	7.03 [82.7]	−28.4	(*R*)	2.02 [50.5]	−68.4
40[e)]	(*R*)·(*R*)	7.11 [83.6]	−33.0	(*R*)	2.05 [51.3]	−87.7
50[e)]	(*R*)·(*R*)	6.97 [82.0]	−37.2	(*R*)	1.99 [49.8]	−99.2
60[e)]	(*R*)·(*R*)	7.06 [83.1]	−42.2	(*R*)	2.08 [52.0]	−110
60[f)]	(*S*)·(*S*)	6.91 [81.3]	+42.2	(*S*)	1.92 [48.0]	+110
70[e)]	(*R*)·(*R*)	5.97 [70.2]	−42.0	(*R*)	1.62 [40.5]	−110
80[e)]	(*R*)·(*R*)	5.41 [63.6]	−42.2	(*R*)	1.54 [38.5]	−110
80[f)]	(*S*)·(*S*)	5.10 [60.0]	+42.2	(*S*)	1.45 [36.3]	+110
90[e)]	(*R*)·(*R*)	3.77 [44.4]	−42.2	(*R*)	1.04 [26.0]	−110

a) Conditions: CYA, 30.0 mmol; GLA·H_2O, 30.0 mmol; (*R*)- or (*S*)-TA, 30.0 mmol; the mixture of acetic acid (9 cm^3) and ethanol (13.5 cm^3) was employed as the solvent; reaction period, 2 h. *b*) (*R*)-2-THC·(*R*)-TA and (*S*)-2-THC·(*S*)-TA salts were represented as (*R*)·(*R*) and (*S*)·(*S*). *c*) The yields were calculated based on the amount (30.0 mmol) of CYA. *d*) $[\alpha]_D^{20}$ (*c*=0.100, pyridine). *e*) (*R*)-TA was employed as the resolving agent. *f*) (*S*)-TA was employed as the resolving agent.

CYA; $[\alpha]_D^{20}$ −110 (*c*=0.100, pyridine). The (*S*)-2-THC·(*S*)-TA salt obtained by the reaction at 60 °C afforded enantiopure (*S*)-2-THC in a yield of 48%; $[\alpha]_D^{20}$ +110 (*c*=0.100, pyridine).

Experimental

General Specific rotations were measured at 589 nm and 20 °C with a Horiba Seisakusho SEPA-300 auto polarimeter equipped with a quartz cell with a 10.0 cm path length. IR spectra were obtained in the range of 4000—400 cm^{-1} with a Perkin-Elmer Model 1600 FT-IR spectrometer by the KBr disk method. ^{1}H- and ^{13}C-NMR spectra were recorded on a JNM-FX270 FT NMR system in DMSO-d_6 with tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in δ units downfield from TMS. Powder X-ray diffraction patterns were obtained with a MAC Science MXP powder X-ray diffractometer with Cu radiation and a graphite monochromater. Melting points were measured with a Yanaco MP-500 D micro melting point apparatus.

CYA was purchased from Tokyo Chemical Ind., Co., Ltd. and was recrystallized from ethanol. (*R*)-4-THC was synthesized by reacting L-cysteine (L-Cys) with formaldehyde.[12] (*R*)-4-THC: $[\alpha]_D^{20}$ −141 (*c*=0.500, water), $[\alpha]_D^{20}$ −139 (*c*=0.100, pyridine). L-Cys was obtained from L-Cys hydrochloride, purchased from Wako Pure Chemicals Ind. (2*R*,4*R*)- and (2*S*,4*R*)-TDA were synthesized by reacting L-Cys with GLA·H_2O.[9] (2*R*,4*R*)-TDA: $[\alpha]_D^{20}$ −180 (*c*=1.00, DMSO), $[\alpha]_D^{20}$ −189 (*c*=0.100, pyridine). (2*S*,4*R*)-TDA: $[\alpha]_D^{20}$ −37.2 (*c*=1.00, DMSO), $[\alpha]_D^{20}$ −17.7 (*c*=0.100, pyridine).

(*RS*)-2-THC CYA (2.31 g, 30.0 mmol) and GLA·H_2O (2.76 g, 30.0 mmol) were added to the mixture of acetic acid (9 cm^3) and ethanol (13.5 cm^3). After stirring the mixture for 3 h at 30 °C, the precipitated (*RS*)-2-THC was collected by filtration, washed thoroughly with ethanol, and dried.

(*RS*)-2-THC: Yield 3.54 g (88.5%); mp 179—181 °C (dec.) (181—182 °C (dec.)).[4] IR (KBr) cm^{-1}: 3044, 2363, 1626, 1448, 1369, 1339, 1314, 1271, 1189, 1145, 911, 875, 740, 706, 611, 579, 521. ^{1}H-NMR (270 MHz, DMSO-d_6, TMS) δ: 4.84 (1H, s, >C<u>H</u>COOH), 3.41—3.32 (1H, m, –CH_2C<u>H</u>HS–), 3.04—2.95 (1H, m, –CH_2CH<u>H</u>S–), 2.84—2.73 (2H, m, –CH_2C<u>H</u>$_2$NH–). ^{13}C-NMR (270 MHz, DMSO-d_6) δ=172.0 (–COOH), 66.4 (–S<u>C</u>H(COOH)NH–), 52.8 (–CH_2<u>C</u>H_2–NH–), 34.5 (–S<u>C</u>H_2CH_2–). XRD *d* nm (rel. int. %): 0.509 (100), 0.385 (85), 0.397 (46), 0.328 (40). *Anal*. Calcd for $C_4H_7NO_2S$: C, 36.08; H, 5.30; N, 10.52. Found: C, 36.13; H, 5.10; N, 10.42.

(*R*)- and (*S*)-2-THC CYA (2.31 g, 30.0 mmol), GLA·H_2O (2.76 g, 30.0 mmol), and (*R*)-TA (4.50 g, 30.0 mmol) were added to the mixture of acetic acid (9 cm^3) and ethanol (13.5 cm^3). After stirring the mixture for 2 h at 30—90 °C, the precipitated (*R*)-2-THC·(*R*)-TA salt was collected by filtration, washed thoroughly with ethanol, and dried. Triethylamine (0.494 cm^3 g^{-1}) was added to the suspension of the salt in methanol (35 cm^3 g^{-1}). After stirring the mixture for 1 h at room temperature, (*R*)-2-THC was collected by filtration, washed with methanol, and dried. (*S*)-2-THC was obtained using (*S*)-TA, as the resolving agent, in a manner similar to that used for (*R*)-2-THC.

(*R*)-2-THC·(*R*)-TA salt obtained at 60 °C: Yield 7.06 g (83.1%); mp 154—155 °C (dec.); $[\alpha]_D^{20}$ −42.2 (*c*=0.100, pyridine). IR (KBr) cm^{-1}: 3318, 2364, 1720, 1560, 1412, 1311, 1266, 1213, 1135, 1069, 790, 688, 573, 490. ^{1}H-NMR (270 MHz, DMSO-d_6, TMS) δ: 4.84 (1H, s, >C<u>H</u>COOH), 4.31 (2H, s, –C<u>H</u>(OH)COOH), 3.41—3.32 (1H, m, –CH_2C<u>H</u>HS–), 3.04—2.95 (1H, m, –CH_2CH<u>H</u>S–), 2.84—2.76 (2H, m, –CH_2C<u>H</u>$_2$NH–). ^{13}C-NMR (270 MHz, DMSO-d_6) δ=173.2 (–CH(OH)<u>C</u>OOH), 172.0 (–CH(NH–)<u>C</u>OOH), 72.2 (–<u>C</u>H(OH)COOH), 66.3 (–S<u>C</u>H(COOH)NH–), 52.8 (–CH_2<u>C</u>H_2–NH–), 34.5 (–S<u>C</u>H_2CH_2–). *Anal*. Calcd for $C_8H_{13}NO_8S$: C, 33.92; H, 4.63; N, 4.94. Found: C, 33.81; H, 4.40; N, 4.99.

(*S*)-2-THC·(*S*)-TA salt obtained at 60 °C: Yield 6.91 g (81.3%); mp 153—155 °C (dec.); $[\alpha]_D^{20}$ +42.2 (*c*=0.100, pyridine). The ^{1}H- and ^{13}C-NMR, and IR spectra were virtually identical to those of (*R*)-2-THC·(*R*)-TA salt. *Anal*. Found: C, 33.68; H, 4.38; N, 4.92.

(*R*)-2-THC obtained at 60 °C: Yield 2.08 g (52.0%); mp 174—176 °C (dec.); $[\alpha]_D^{20}$ −110 (*c*=0.100, pyridine). IR (KBr) cm^{-1}: 3215, 2361, 1626, 1483, 1434, 1359, 1328, 1292, 1200, 869, 840, 720, 648, 576, 518. The ^{1}H- and ^{13}C-NMR spectra were virtually identical to those of (*RS*)-2-THC. XRD *d* nm (rel. int. %): 0.490 (100), 0.349 (59), 0.458 (45), 0.358 (35). *Anal*. Found: C, 36.01; H, 5.10; N, 10.45.

(*S*)-2-THC obtained at 60 °C: Yield 1.92 g (48.0%); mp 174—176 °C (dec.); $[\alpha]_D^{20}$ +110 (*c*=0.100, pyridine). The ^{1}H- and ^{13}C-NMR spectra were virtually identical to those of (*RS*)-2-THC and IR spectrum and powder X-ray diffraction pattern to those of (*R*)-2-THC. *Anal*. Found: C, 35.92; H, 5.07; N, 10.24.

Rate Constant of Racemization After rapidly dissolving (*R*)-2-THC (0.0500 g) in 10 cm^3 of acetic acid at 20, 25, 30 and 35 °C, the optical rotation of the solution was measured at 589 nm, appropriate intervals, and 20, 25, 30 and 35 °C. The rate constants of racemization (k_R(s^{-1})) were calculated by the least-squares method from

$$\ln \alpha_o/\alpha_t = k_R \cdot t,$$

where α_t is the optical rotation at time *t* and α_o the optical rotation extrapolated to time zero. The rate constant was also measured in water at 20 °C by a method similar to that in acetic acid.

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