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Kazuki Sada[ab]; Kazunori Nakano[ac]; Kiyoshi Hirayama[a]; Mikiji Miyata[ad]; Satoshi Sasaki[b]; Kiichi Takemoto[b]; Nobutami Kasai[b]; Kazuaki Kato[d]; Masashi Shigesato[d]; Kunio Miki[e]
[a] Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido Gifu, Japan [b] Department of Applied Chemistry and Applied Fine Chemistry, Faculty of Engineering, Osaka University, Osaka, Japan [c] Nagoya Municipal Industrial Research Institute, Nagoya, Japan [d] Department of Material and Life Science, Graduate School of Engineering, Osaka University, Osaka, Japan [e] Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Japan

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Molecular Recognition of Medium-size Lactones by Enclathration of Cholic Acid

KAZUKI SADA[a,b,*], KAZUNORI NAKANO[a,†], KIYOSHI HIRAYAMA[a], MIKIJI MIYATA[a,c], SATOSHI SASAKI[b], KIICHI TAKEMOTO[b], NOBUTAMI KASAI[b], KAZUAKI KATO[c], MASASHI SHIGESATO[c] and KUNIO MIKI[d]

[a]*Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido Gifu 501-1112, Japan;*
[b]*Department of Applied Chemistry and Applied Fine Chemistry, Faculty of Engineering, Osaka University;*
[c]*Department of Material and Life Science, Graduate School of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan;*
[d]*Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-oiwake-cho, Sakyo, Kyoto 606-0745, Japan*

Molecular recognitions of medium size lactones by enclathration of cholic acid (CA) are described. Size and location of the substituents on the lactone rings play an important role for enclathration. Lactones within the limited steric dimensions are included in CA, and larger or smaller ones are not included to give guest-free crystals of CA. Moreover, CA partially separates one enantiomer from racemic lactones by recystallization. X-ray crystallographic studies reveal that all included lactones form the β-trans type bilayer structure having a pentagonal void channel with a side pocket. The cross-sections illustrate that the lactone rings are incorporated in the center of the channel and that the substituents of the guests are fixed in the side pockets. The asymmetric channel enables CA to discriminate size and chirality of medium size lactones.

Keywords: Molecular recognition; Enclathration; Cholic acid; Lactone; Host-guest; Crystal structures

INTRODUCTION

Considerable interest in crystalline inclusion compounds has arisen during the past decade due to their high specificity for guest recognition [1], and especially, their ability to achieve optical resolution of racemic compounds on preparative scales. One of the earliest examples is the optical resolution of tertiary acetylenic alcohols by brucine [2]. Since then, many host compounds have been found and used as chiral-resolving reagents [3–12]. For example, tertiary acetylenic alcohols by sparteine [3], sulfoxides by bis-β-naphthol [4] and (*R*)-phenylglycyl-(*R*)-phenylglycine [5], aliphatic secondary alcohols by some alkaloids [6], tartrate hosts [7], tartrate esters [8] and cholamide [9], cyclic ketones and lactones by acetylenic alcohols [10] and lactate derivatives [11], and so on, have been reported. However, there have been a few reports of mechanistic studies of chiral recognition on the basis of determination of scope and limitation of guest candidates as well as extensive structural investigations of the host frameworks. Green *et al.*, have extensively examined chiral discriminations of a series of 2-substituted butanes by tri-*o*-thymotide [12].

*Address for correspondence: Department of Material & Life Science, Graduate School of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan.
†Present Address: Nagoya Municipal Industrial Research Institute, Rokuban, Atsuta-ku, Nagoya 456-0058, Japan.

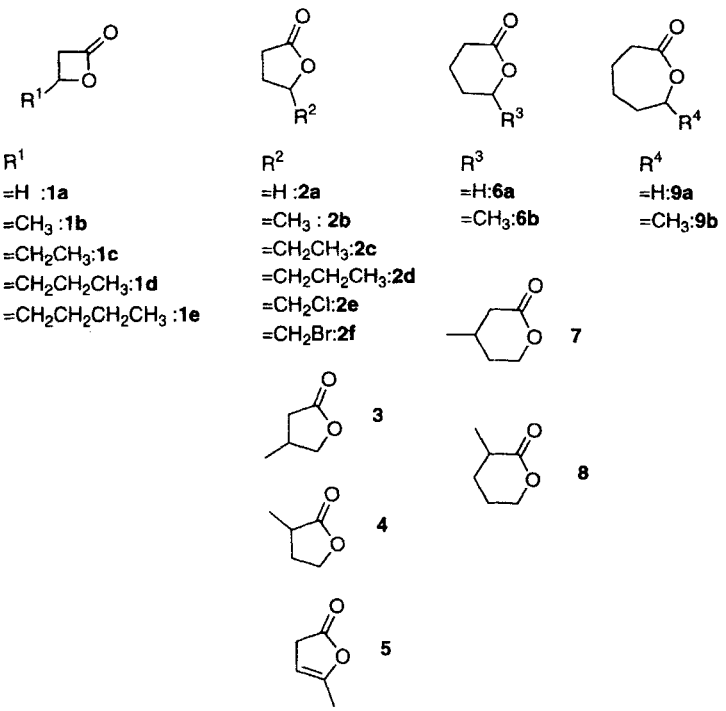

CHART 1 Medium-size lactones.

Steroidal bile acids are complex natural compounds produced in the liver of vertebrate animals from cholesterol. Discovery of molecular complexes in crystalline state dates back to the end of the nineteenth century [13]. Deoxycholic acid (3α, 12α-dihydroxy-5β-cholan-24-oic acid, **DCA**) is one of the classical host molecules to form channel-type inclusion compounds with a variety of organic compounds [14]. More recently, we found that cholic acid (3α,7α,12α-trihydroxy-5β-cholan-24-oic acid, **CA**) forms channel-type inclusion compounds with various organic substances [15]. X-ray crystallographic studies of **CA** inclusion crystals revealed that they have a bilayer structure with molecular channels, for aromatic compounds [16] and aliphatic esters [17], and a crossing structure with caged cavities for alcohols [18] and nitriles [19]. The asymmetric host compound is expected to have asymmetric molecular cavities, which enables chiral discrimination for many racemic organic compounds [20,21]. In this paper, we describe size and chiral recognitions

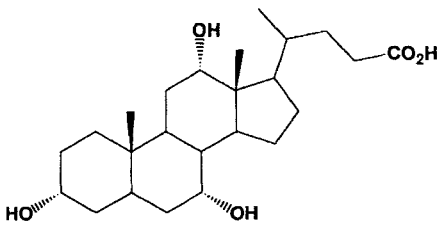

FIGURE 1 Molecular structure of cholic acid(**CA**).

of medium-size lactones, shown in Chart 1, by enclathration of **CA**. Moreover, the systematic investigations of the crystal structures and cross sections of the channels provide rationale for molecular recognitions of lactones [21].

RESULTS AND DISCUSSION

Formation of Inclusion Crystals

Recrystallization of **CA** from medium-size lactones gives transparent CA crystals. Table I summarizes results of formation of inclusion crystals with various medium-size lactones.

TABLE I Host–guest ratios and release temperatures of inclusion crystal of **CA** with lactones

Lactones	Host : guest ratios[a]	Release temp. (°C)[a]
1a	NG[b]	–
1b	1 : 1	90
1c	1 : 1	106
1d	1 : 1	93
1e	NG	–
2a	NG	–
2b	1 : 1	128
2c	1 : 1	119
2d	NG	–
2e	1 : 1	129
2f	NG	–
3	1 : 1	91
4	1 : 1	104
5	1 : 1	–
6a	NG	–
6b	1 : 1	113
7	1 : 1	110
8	NG	–
9a	1 : 1	115
9b	NG	–

[a] Determined by TGA.
[b] NG = No host–guest crystals.

Host–guest ratios in the inclusion crystals all are strictly 1 : 1 by the weight-loss on TGA and integration of the solution ^{1}H-NMR.

It is noteworthy that **CA** forms inclusion crystals with the specific lactones. Among 5-membered lactones, **2b**, **2c**, **2e**, **3**, and **4** are included, while **2a** and **2d** are not. Similar discrimination is observed in a series of 4-membered lactones. β-Substituted-β-lactones with medium substituents (**1b**, **1c**, and **1d**) form stable inclusion crystals, but unsubstituted (**1a**) or *n*-butyl-substituted (**1e**) are not incorporated. The size of the substituents plays an important role for enclathration.

Moreover, **CA** clathrates exhibit chiral discrimination of lactones having an asymmetric carbon. All lactones are partially resolved by the single recrystallization from racemic mixture. Table II shows predominant configurations and enantiomeric excesses (e.e.%) of the lactones recovered from the inclusion crystals by distillation. Enantiomeric excesses are around 40%e.e. and depend on the substituents. The lowest value for the smallest guest may be understood in terms of misfit to the host cavity. The absolute configurations of the included lactones are assigned as (*S*)-isomers in all lactone complexes by polarimetry and X-ray crystallography. Therefore, the host channel has steric complementary to (*S*)-isomers rather than (*R*)-isomers.

TABLE II Enantioselective inclusion of **CA** with lactones

Lactones	ee%[a]
1b	19(S)
1c	36(S)
1d	41(S)
2b	42(S)
2c	34(S)
5b	53(S)

[a] In parenthesis, predominant configurations are shown.

Host Frameworks of CA

X-ray structural analyses of eight lactone complexes (**1b**, **1c**, **2b**, **2c**, **4**, **5**, **6b**, and **9a**) were performed. The crystallographic data are summarized in Table III, and the crystal structures are depicted in Figure 2. The facially amphiphilic molecular structure of **CA** allows a bilayer structure to be formed by van der Waals association of the lipophilic β-faces and hydrogen bonding between the α-hydrophilic faces. In the hydrophilic layers, a cyclic hydrogen bond network links the steroid molecules to yield a two-dimensional layer structure. The layers stack by the van der Waals force and steric complementary between them. The anchored molecular shape of **CA** makes the layer corrugated, and the offset stacking of the lipophilic faces yields one-dimensional host cavities in the lipophilic layers. All lactones are included in a β-trans type host framework, which is distinguished on the basis of the trans-conformation of the side chain and the stacking manner in the lipophilic layers [15b]. This host framework is same as those of **CA** with aliphatic small esters [17].

TABLE III Crystallographic data of **CA** with lactones

	CA · 1b	**CA · 1c**	**CA · 2b**	**CA · 2c**	**CA · 4**	**CA · 5**	**CA · 6b**	**CA · 9a**
Formula	$C_{28}H_{46}O_7$	$C_{29}H_{48}O_7$	$C_{29}H_{48}O_7$	$C_{30}H_{50}O_7$	$C_{29}H_{48}O_7$	$C_{29}H_{46}O_7$	$C_{30}H_{50}O_7$	$C_{30}H_{50}O_7$
Formula weight	494.67	508.69	508.69	522.72	508.69	506.68	522.72	522.72
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a (Å)	12.632(1)	12.6995(4)	12.902(3)	12.6995(4)	12.9908(9)	12.7507(2)	13.0491(5)	13.3571(7)
b (Å)	7.9311(7)	8.0371(2)	7.965(1)	8.1639(3)	7.9443(5)	8.0002(1)	8.0762(3)	7.9667(5)
c (Å)	14.030(1)	14.0545(4)	13.969(3)	14.0220(6)	13.949(1)	14.096(3)	13.8668(6)	13.896(1)
β (deg)	103.777(3)	103.941(1)	104.394(8)	104.079(2)	104.021(3)	105.19(1)	104.146(2)	106.555(3)
V (Å^3)	1365.1(2)	1392.24(7)	1390.5(5)	1419.0(1)	1396.7(2)	1387.7(3)	1417.07(10)	1417.4(2)
Z	2	2	2	2	2	2	2	2
D_c(g/cm^3)	1.203	1.213	1.215	1.223	1.210	1.213	1.225	1.225
Observed reflections ($I > 2\sigma$)	2606	2607	2516	2621	2511	2647	2607	2649
R[a]	0.082	0.062	0.051	0.060	0.060	0.068	0.046	0.045
R_w[b]	0.209	0.150	0.110	0.126	0.156	0.109	0.125	0.096
GOF	2.15	1.88	1.86	1.97	1.96	1.98	1.79	1.57
2θmax (deg)	136.5	136.4	136.5	136.4	136.5	136.4	136.5	136.5
R/P	7.73	8.00	7.72	7.82	7.70	8.12	7.64	7.90
Temperature (°C)	−75	−75	−75	−75	−75	−75	−75	−75

[a] $R = \Sigma\{||F_o| - |F_c||/|F_o|\}$.
[b] $R_w = \{\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2\}^{1/2}$.

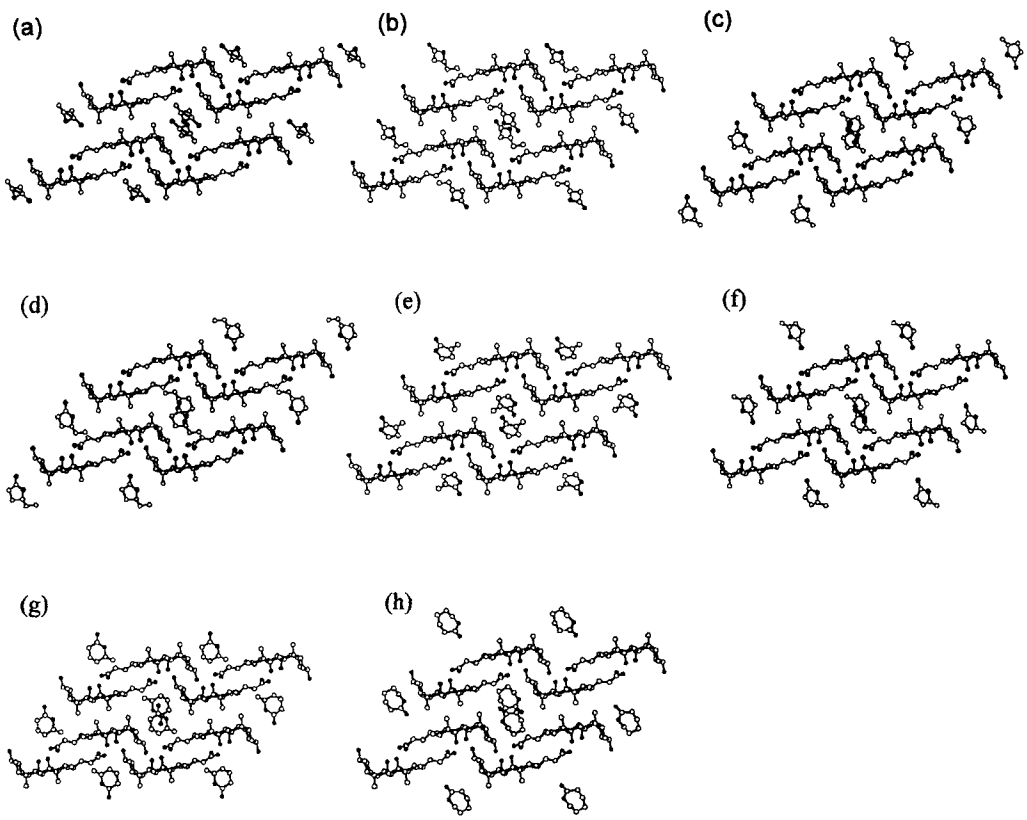

FIGURE 2 Crystal structures of inclusion crystals of **CA** with (a) **1b**, (b) **1c**, (c) **2b**, (d) **2c**, (e) **4**, (f) **5**, (g) **6b**, and (h) **9a**. Oxygen and carbon atoms are represented by solid and empty circles, respectively. Hydrogen atoms are omitted for clarity.

Since the hydrogen bond donors of the host components are used in the intramolecular host–host hydrogen bond network, there is no hydrogen bonding between the host and the guest. This indicates that the guest components are entrapped by steric dimensions and van der Waals force. In order to study the specific recognitions of the host frameworks of **CA**, we investigated the host cavities by cross-sectional views of the channels.

Molecular Channels and Guest Recognitions

Comparison of steric dimensions between the guest molecules and the host cavities may provide the explanation for selective enclathration. Computer-aided 'molecular tomograms', cross-sections of space filling models, can visualize steric dimensions of the host cavities and are useful for the elucidation of molecular recognition of guest compounds [22]. Figure 3 shows the crystal structure of **CA** · **2c** viewed from three different directions and slicing planes for the cross-sections. Figures 4a, 4b and 4c represent the cross-sections sliced at the solid line, the break line, and the double solid line in Figure 3, respectively.

The cross-section of the host channel is shown in Figure 4a. The channel is surrounded by five different parts of five different host compounds, which yields a deformed pentagonal shape as a unit in the cross-section. This shape enables the medium-size lactones to be included in the perpendicular to the direction of the host channel, and the guest components stack in the host channel.

The requirement for a methyl group in the guest lactones is explained by the role of a side pocket of the host channel. The side pocket is

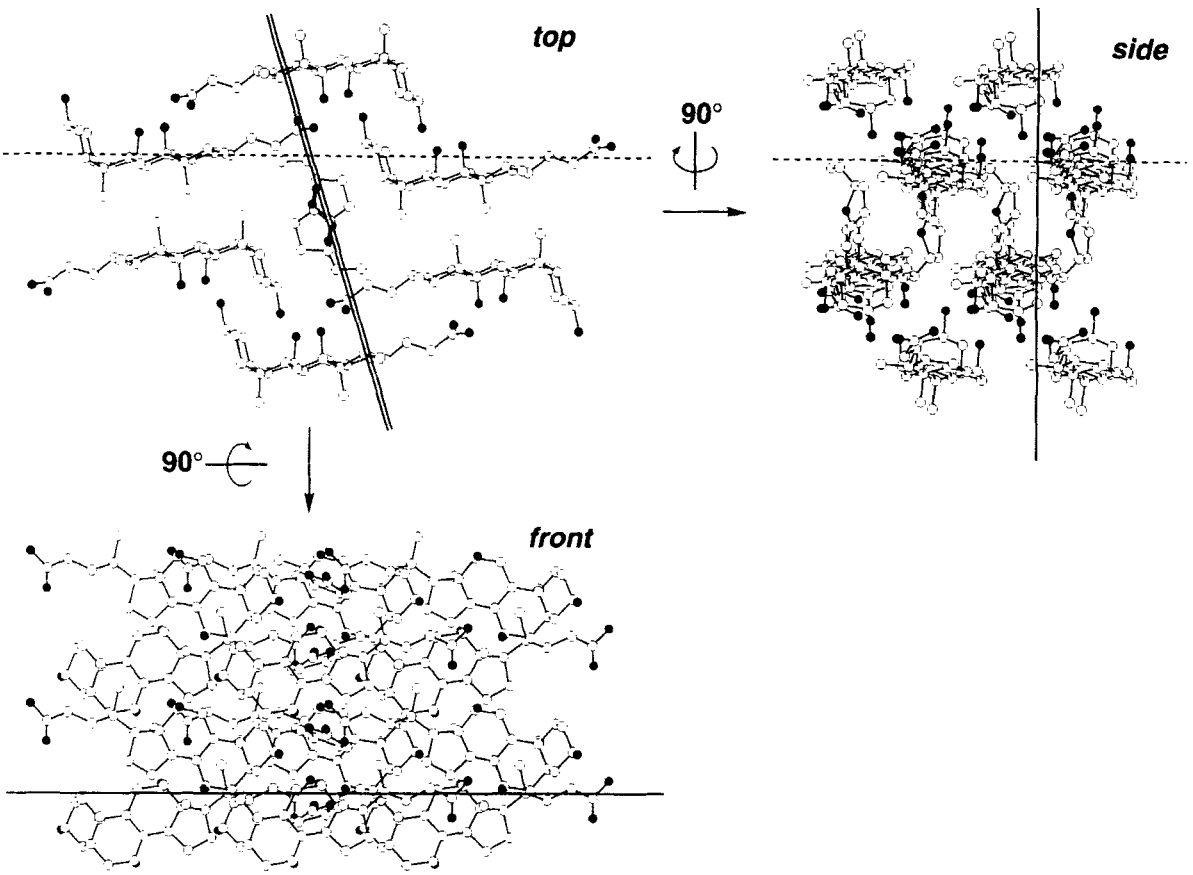

FIGURE 3 Crystal structures of **CA** · **2c** viewed from three directions. Oxygen and carbon atoms are represented by solid and empty circles, respectively. Hydrogen atoms are omitted for clarity.

constructed by structural disparity between the wide steroid plane and the flexible thin side chain, as shown in Figures 4b and 4c. Namely, between the side chains of neighboring host molecules, a small void groove spirals along the host channels. It can be seen that the lactone rings are accommodated in the main part of the host channel and that the substituents are included in the side pocket. Therefore, unsubstituted lactones, except **8**, do not fit the side pocket. Moreover, the size of the side pocket is similar to those of the ethyl group. Guest candidates that have larger than the ethyl group are not accommodated in **CA**. Among the unsubstituted lactones, only **8** is incorporated. X-ray crystallography shows that **8** in the channel have the chair conformation. A carbon atom adjacent to the ester group is coplanar to the ester moiety. The other ring carbon atoms protrude from the carboxyl plane and act just like the substituents of **2b** or **5b**. The planner structure of other unsubstituted lactones may be unstable in the host channel of **CA**. As a result, the steric fit between the substituents and the side pocket plays an important role in the formation of inclusion crystals. The lactones with larger or smaller substituents form the unstable complexes.

The molecular tomography also provides an explanation for the chiral discrimination of some lactones. The side pocket is tilted from the crystallographic *ac*-plane along the twofold screw axis, as shown in Figure 4c. This enables

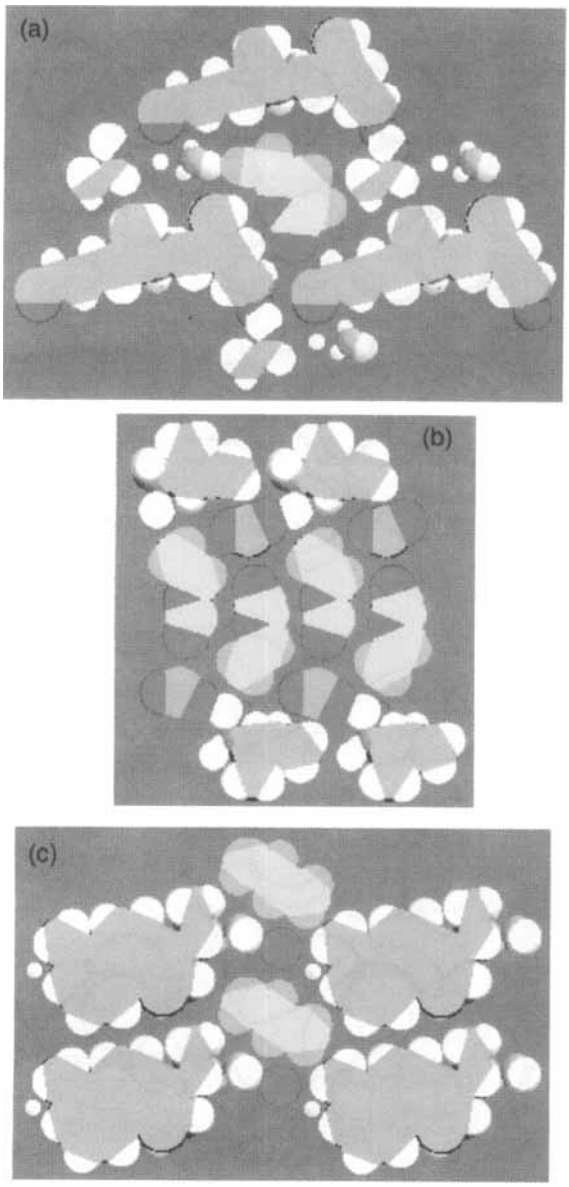

FIGURE 4 Cross-sections of space-filling models of **CA** · **2c** sliced at (a) the solid line perpendicular to the crystallographic *b*-axis, (b) the break line parallel to the crystallographic *b*-axis, and (c) the double solid line parallel to the crystallographic *b*-axis in Figure 3, respectively. Oxygen atoms are colored red. Carbon atoms and hydrogen atoms of the host compounds are colored grey and white, respectively. Those of the guest compounds are yellow and blue, respectively. (See Color Plate I).

to the helical groove on the surface of the host channels. This helical side pocket causes the stereoselection of lactones. When the ethyl group of (*R*)-**2c** is hypothetically enclosed in the side pocket, the lactone ring must be oriented parallel to the direction of the channels and cannot stack along the crystallographic *b*-axis, as shown in Figure 5. Moreover, the ethyl group in this orientation is too thick for the side pocket to fill it. Therefore, the steric complementary of (*S*)-**2c** to the host cavity is much better than that of (*R*)-**2c**.

EXPERIMENTAL SECTIONS

General Methods

IR spectra were recorded on a JASCO IR-810 or a JASCO IR Report 100 grating spectrometer using a KBr disk. ^{1}H-NMR spectra were recorded on a JEOL 270 MHz FT-NMR spectrometer, and chemical shifts are reported in parts per million (ppm) from tetramethylsilane. Theromogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured by a Rigaku Thermoflex TG 8110 instrument. GLC analysis was carried out by a Shimadzu GC6A instrument. Analyses by HPLC were carried out by a Shimadzu 9C series or a Toso CCPD liquid chromatograph. Operating parameters varied a little, but the following were typical: Dicel chiralcel OB column, 250 × 2 mm i.d., *n*-hexane/isopropanol = 9/1. Optical rotation was carried out on a Photal PM-201A instrument. The microdistillation was carried out using a Shibata GTO-250RS micro glass-tube oven.

Materials

All solvents and chemicals were of reagent grade quality, purchased commercially and used without further purification. β-Hexalactone (**1c**) [23], β-heptalactone (**1d**) [23], β-octalactone (**1e**) [23], δ-chloro-γ-valerolactone (**2e**) [24], δ-bromo-γ-valerolactone (**2f**) [25], β-methyl-γ-butyrolactone (**3**) [26], α-methyl-γ-butyrolactone (**4**) [27], δ-hexalactone (**6b**) [28], and

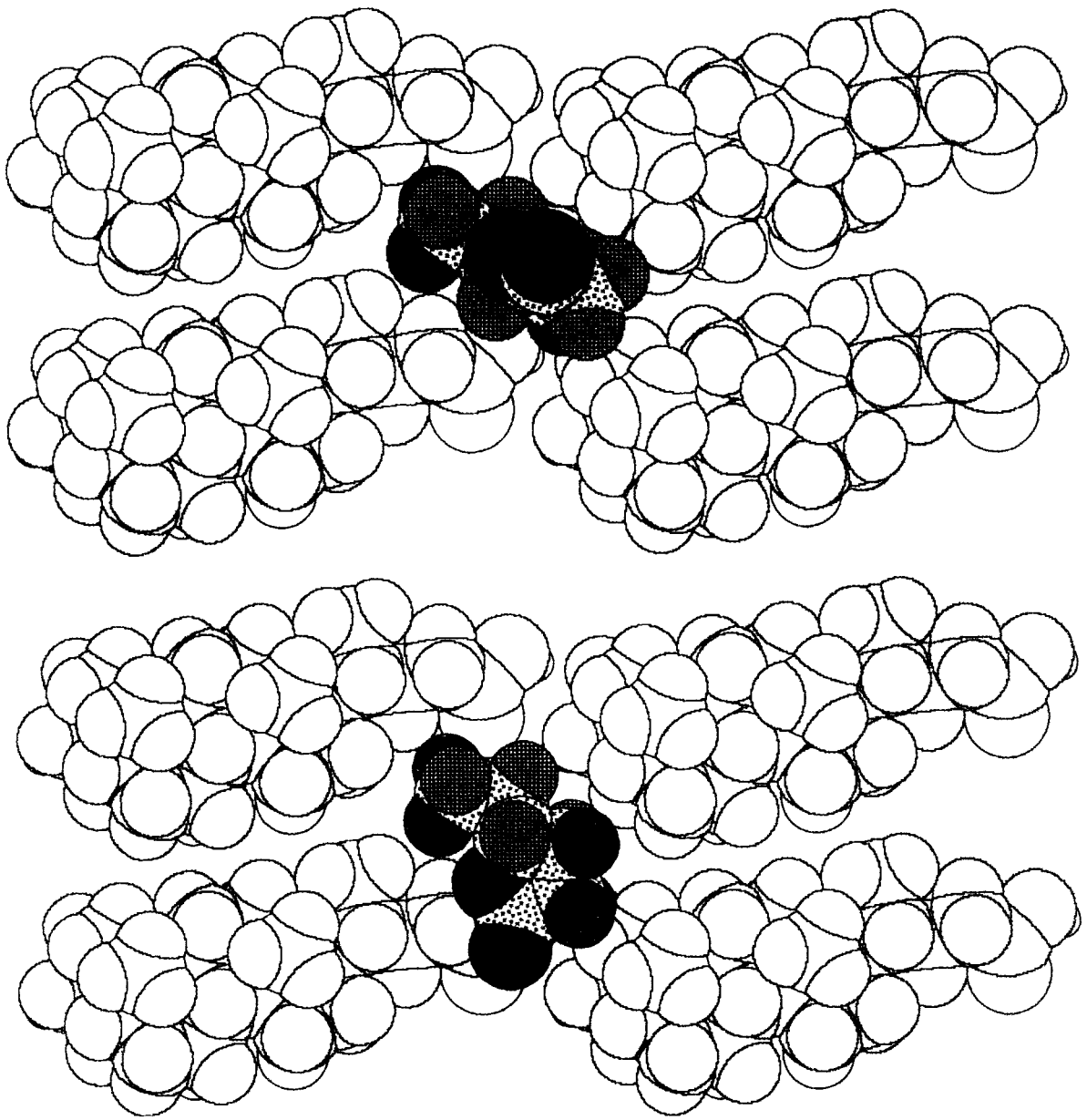

FIGURE 5 Schematic representation of the accommodation of the ethyl group of (a) (*R*)-**2c** and (b) (*S*)-**2c** in the side pocket of the host channel.

3-methyl-δ-valerolactones(**7**) [29] were prepared according to the literature.

Preparation of Inclusion Crystals

Preparation of inclusion crystals usually consists of recrystallization of the cholic acid from neat guest candidates or a mixture of 1-butanol and lactones. In the latter method, cholic acid (0.5 g) was dissolved in 3.0 mL of γ-valerolactone (**2b**) heated to 130°C. The solutions were allowed to cool to room temperature until crystals began to form. Cholic acid crystals were collected and air-dried upon a filter paper for several minutes. In

the former method, cholic acid (0.5 g) was dissolved in 3.0 mL of 1-butanol, and guest lactones were added at room temperature. The solutions were allowed to cool to room temperature until crystals began to form.

Determination of Optical Purity

The lactones included in the host lattice were collected by micro-distillation under reduced pressure. Enantiomeric excesses of the isolated guests were determined by a chiral HPLC column or ^{1}H-NMR studies by using (*R*)-2,2,2-trifluoro-1-(9-anthryl)ethanol as the chiral shift reagent.

Crystal Structure Determinations

X-ray diffraction data were collected on a Rigaku RAXIS-RAPID diffractometer with 2D-area detector with graphite-monochromatized Cu-Kα radiation. Lattice parameters were obtained by least-squares analysis from reflections of three oscillation images. Direct methods (SIR92) were used for the structure solution. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and no further refinement was applied. The structure was refined by the full matrix least-squares procedure. All calculations were performed using the TEXSAN [30] crystallographic software package. The measurement conditions and structural details are listed in Table III.

Molecular Graphics

Molecular 'tomographic' drawings were generated on the NEC PC 9801 or Apple computers with the molecular drawing graphic software based on MODRASTE [22], which can generate cross-sectional views of molecules sliced centered at arbitrary positions along all of the direction with arbitrary thickness. We modified this software to be suitable for molecular assemblies. Firstly, we built one unit of the channel consisting of the 18 host–guest pairs on the basis of the fractional atomic coordinates from X-ray crystallography. The bodies of the host–guest complexes were sliced at a thickness of 0.2 Å in various directions. Van der Waals radii of hydrogen, oxygen, and carbon atoms for the space filling models in MODRASTE are fixed at 1.20 Å, 1.60 Å, and 1.45 Å, respectively.

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