IR spectra were recorded on a Perkin-Elmer 700 spectrometer. VPC studies were carried out on a Varian 920 preparative gas chromatograph by using a 6 ft × 0.25 in. SE-30 on Chromosorb P column.

Kinetic Studies. The following general procedure was employed. Compound 1 (20 mg, 0.055 mmol) was added, as the solid, to 500 μL of $CDCl_3$ (Merck; no Me_4Si) containing 1 μL of *cis*-3-hexene[6] in a new 5-mm NMR tube. Anisole (5 μL) was added as an internal standard. The NMR spectrum was recorded, and the signals were electronically integrated. The desired amount of alkene was added, via syringe, to the solution at 34 °C and mixed by inverting the tube. Runs were carried out with 1-fold, 3–4-fold, and 7–10-fold excesses of each alkene relative to 1. Runs with a 15–20-fold excess of alkene to 1 were carried out for the less reactive alkenes. The signals were recorded and integrated vs. time. The rates of appearance of 2 and oxirane were checked and found to correspond to the rate of disappearance of 1. Final product yields of 2 and oxirane were determined relative to the internal standard. For example, the yields of 2 and oxirane were 55% and 60% for the reaction of 1 with 1 equiv of 2,3-dimethyl-2-butene but increased to 90% and 94%, respectively, for a reaction with a 7-fold excess of the alkene. Pseudo-first-order plots of the relative concentration of 1 were linear for at least 2 half-lives. The second-order rate constants were determined by dividing the observed pseudo-first-order rate constants by the initial alkene concentrations. A 2-fold variation in the concentration of 1 in the presence of a large excess of alkene did not affect the observed pseudo-first-order rate constant. A 3-fold variation in the alkene concentration resulted in a 3-fold variation in k_{obsd} while the calculated second-order rate constants were within experimental error of each other (±10%).

Product Studies. Compound 2 (mp 93–94 °C) was isolated (crystallization at −20 °C) from the reaction mixtures in ~30% yield by partial removal of the solvent at reduced pressure followed by addition of pentane. The structural proof for 2 has been reported.[5] The NMR spectra of the completed reaction mixtures showed the epoxides to be present in all cases. The yield of epoxide for each reaction was confirmed by gas chromatography. The epoxides from the 2,3-dimethyl-2-butene and the cyclopentene cases were isolated by preparative gas chromatographic techniques and proven to be identical with authentic samples by comparison of spectral data. Authentic samples of the oxiranes were prepared by the reaction of the corresponding alkenes with 1 equiv of *m*-chloroperbenzoic acid.

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Registry No. 1, 76847-41-1; 2, 76847-42-2; 2,3-dimethyl-2-butene, 563-79-1; 1,2-dimethylcyclohexene, 1674-10-8; 2-methyl-2-butene, 513-35-9; 1-methylcyclohexene, 591-49-1; cyclopentene, 142-29-0.

Polymeric Inclusion Compound Derived from β-Cyclodextrin

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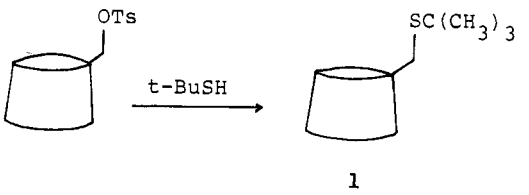
Cyclodextrins have received much attention as relatively low molecular weight models for biological macromolecules.[1] This interest has been enhanced by their specific chemical modifications, giving more desirable mimics of enzymes.[2] However, the structures of modified cyclodextrins, even simple monosubstituted cyclodextrins, have never been studied although cyclodextrins[3,4] and their inclusion complexes[5-8] with various guest molecules have been extensively studied by X-ray analysis. Moreover, there is no direct evidence concerning the existence of

Scheme I



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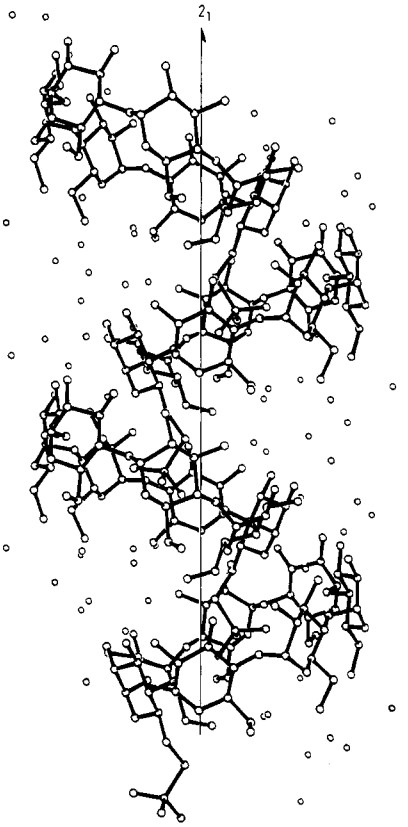

Figure 1. Drawing of a novel helical polymer penetrated by the 2_1 screw axis which is parallel to the *c* axis and shown by a long straight line. The *t*-BuS group is intermolecularly included in the hydrophobic cavity of the macrocycle. Water oxygen atoms are represented by smaller circles.

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0022-3263/82/1947-1143$01.25/0

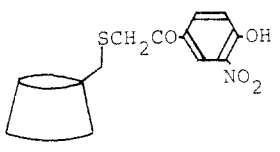
inclusion complexes between guests and substituted cyclodextrins, while there are many indirect evidences.[1]

In the hydrolyses of substituted phenyl acetates by α- or β-cyclodextrins, meta-substituted phenyl esters were more rapidly hydrolyzed than the corresponding para-isomers, a phenomenon called "meta selectivity".[1] In our previous paper,[9] we demonstrated the disappearance of the selectivity by the introduction of a *tert*-butylthio group instead of a primary hydroxyl group of β-cyclodextrin (1), suggesting the possibility of the partial inclusion of the *tert*-butyl group by the cyclodextrin cavity in the same molecule. However, as the concentration of an aqueous solution of 6-deoxy-6-(*tert*-butylthio)-β-cyclodextrin (1) is increased, an intermolecular inclusion of a *tert*-butyl group by the cyclodextrin cavity of another 1 will be possible to give dimeric, trimeric, etc. and polymeric inclusion compounds. Thus, the structure analysis of this monosubstituted cyclodextrin is quite interesting since it has both characters as host (cyclodextrin moiety) and as guest *tert*-butylthio group).

We report here the X-ray crystallographic study of 1. This is a first structural determination of a monosubstituted cyclodextrin and the first direct evidence concerning the existence of an inclusion complex of a monosubstituted cyclodextrin.

The compound 1 was prepared from the reaction of 6-deoxy-6-(*p*-tosyloxy)-β-cyclodextrin[2e] with *tert*-butyl mercaptan (Scheme I). Repeated recrystallization from water gave pure 1. Beautiful colorless tabular crystals, stable only in the mother liquor, were obtained by keeping the temperature of the solution at 60 °C. As is shown in Figure 1, the molecules are located around the 2_1 screw axis to give an interesting polymeric structure where the *tert*-butylthio group (guest) is intermolecularly included in the hydrophobic cavity of the cyclodextrin moiety (host), directly confirming that the monosubstituted cyclodextrin includes the guest in its cavity. This is also the first polymeric inclusion compound formed from a single species acting both as a guest and as a host. The cyclodextrin moiety has an approximate 7-fold axis and a round shape, demonstrating that the monosubstitution does not particularly alter the structure of the cyclodextrin macrocycle compared with that of the native β-cyclodextrin.[4,7,8]

This X-ray analysis suggests that in solution there may exist not only monomers in which *tert*-butyl groups might be shallowly included intramolecularly in the cavities but also dimers or even higher complexes in concentrated water solution. Actually, the existence of dimers in solution has been preliminarily confirmed in a different system where a hybrid dimer between 6-deoxy-6-[(*p*-hydroxy-*m*-nitrophenacyl)thio]-β-cyclodextrin (2) and β-cyclodextrin was



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spectroscopically measured in the presence of excess β-cyclodextrin,[10] while the (*p*-hydroxy-*m*-nitrophenacyl)thio moiety was found to be shallowly included intramolecularly by the cyclodextrin cavity in concentrations of 2 below 2 × 10^{-4} M.[2e]

The present result suggests that dimeric inclusion in solution and polymeric inclusion in the solid state may reasonably occur in the other monosubstituted cyclodextrins. When the substituents (guests) at the 6-position are suitably selected, there is the possibility of solid-state reactions in one direction along the β-cyclodextrin macrocycle column.[11]

Experimental Section

6-Deoxy-6-(*tert*-butylthio)-β-cyclodextrin (1). A solution of 6-deoxy-6-(*p*-tosyloxy)-β-cyclodextrin[2e] (1.00 g, 0.776 mmol) and *tert*-butyl mercaptan (1.24 g, 13.8 mmol) in 100 mL of degassed aqueous Na_2CO_3 (pH 12) containing 20% ethanol was stirred at 50 °C under a nitrogen atmosphere for 24 h. The solution was acidified with HCl to pH 4, washed with ether (3 × 20 mL), neutralized with NaOH to pH 7, concentrated in vacuo, again acidified to pH 4, and stirred vigorously with trichloroethylene (1 mL) for 12 h. The precipitate was filtered and dissolved in water (10 mL). Concentration in vacuo followed by addition of water was repeated at least four times. The resultant aqueous solution was lyophilized to give white solid (1), 410 mg. A hot (98 °C) solution of 1 (100 mg) in water (50 mL) was gradually cooled to 60 °C, and the temperature of the solution was maintained at 60 °C. After 5 days, the solution was allowed to cool. The crystal formed was collected along with its mother liquor for the X-ray analysis: ^{1}H NMR (D_2O–Me_2SO-d_6) δ 1.18 (s, 9 H, Me), 2.9 (2 H, CH_2S), 3.15–4.0 (40 H, cyclodextrin protons other than C_1 H), 4.81 (7 H, C_1 H). The IR was very similar to that of β-cyclodextrin. Anal. Calcd for $C_{46}H_{78}O_{34}S·H_2O$: C, 45.09; H, 6.58. Found: C, 45.08; H, 6.38.

X-ray Structural Analysis: $C_{46}H_{78}O_{34}S·22H_2O$, orthorhombic, space group $P2_12_12_1$, a = 32.107 (9) Å, b = 15.517 (5) Å, and c = 15.097 (5) Å at −100 ± 2 °C. Intensity data with $2\theta < 44°$ were collected at −100 °C with graphite-monochromated Mo Kα radiation and by using the ω-scan technique under a cold stream of nitrogen. Out of the 5022 data, 1525 were below the 2σ threshold and were considered as unobserved. The structure was solved by the rotation function,[12] R maps, and rigid-body least-squares[13] methods. The structure has now been refined to a current R of 13% by block-diagonal least-squares methods. All atoms except S are isotropic. Thirty-three water molecules were located by difference Fourier syntheses, with site occupancy factors varying from 0.3 to 1.0. Figure 1, prepared with ORTEP-II,[14] illustrates the structure.

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Registry No. 1, 80593-69-7; 6-deoxy-6-(*p*-tosyloxy)-β-cyclodextrin, 67217-55-4; *tert*-butyl mercaptan, 75-66-1.

Supplementary Material Available: Table I listing fractional coordinates and temperature factors for 6-deoxy-6-(*tert*-butylthio)-β-cyclodextrin (4 pages). Ordering information is given on any current masthead page.

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