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Stereoselective Solvolyses of Activated Esters in the Aggregate System of Imidazole-Containing Copolymeric Surfactants

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Stereoselective solvolyses of optically active activated esters in the aggregate system of optically active polymeric surfactants containing imidazole and benzene moieties were performed. The catalyst polymers employed were copolymers of N-methacryloyl-L-histidine methyl ester (MHis) with N,N-dimethyl-N-hexadecyl-N-[10-(*p*-methacryloyloxyphenoxycarbonyl)-decyl]ammonium bromide(DEMAB). In the solvolyses of N-carbobenzoxy-D- and L-phenylalanine *p*-nitrophenyl esters (D-NBP and L-NBP) by polymeric catalysts, copoly (MHis-DEMAB) exhibited not only increased catalytic activity but also enhanced enantioselectivity as the mole % of surfactant monomers in the copolymers increased. The polymeric catalysts showed noticeable enantioselective solvolyses toward D- and L-NBP of the substrates employed. As the reaction temperature was lowered for the solvolyses of D- and L-NBP with the catalyst polymer containing 3.5 mole % of MHis, the increased reaction rate and enhanced enantioselectivity were observed. The coaggregative systems of the polymer and monomeric surfactants were also investigated. In the case of coaggregate system consisted of 70 mole % of cetyldimethylethylammonium bromide with polymeric catalyst showed maximum enantioselective catalysis, *viz.*, $k_{cat}(L)/k_{cat}(D) = 2.85$. The catalyst polymers in the sonicated solvolytic solutions were confirmed to form large aggregate structure by electron microscopic observation.

Introduction

A great many investigations have been performed regarding the possible alteration of reaction rates in organized media such as micelles, vesicles, polyelectrolytes, and macrocyclic hosts.[1-7] In most cases, the hydrophobic interac-

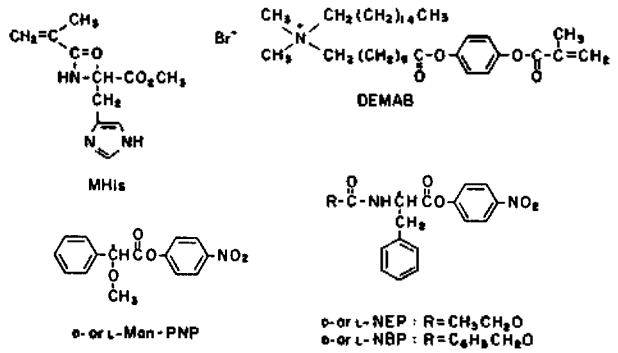


Figure 1. Chemical structures of monomers and substrates.

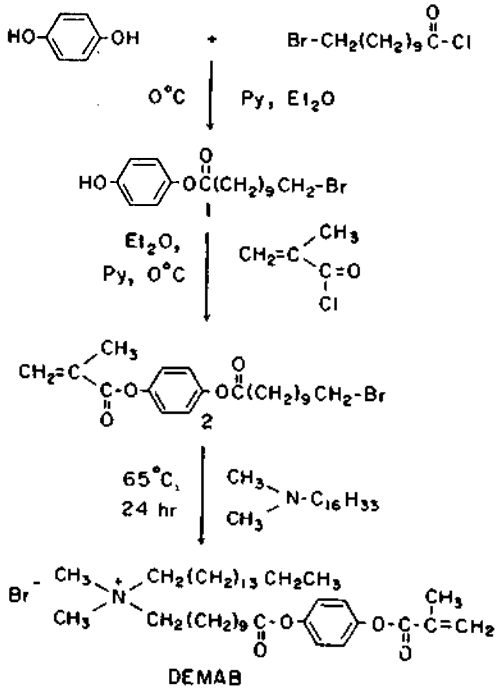
tions in ordered environment are considered to be an important factor in control of reaction rate and for rate enhancement and stereoselectivity particularly in the solvolytic reactions.[2-6, 8-10] Most of reported enantioselective solvolytic studies have, however, been in the micellar or bilayer systems of histidyl peptides of low molecular weight,[11-15] and stereochemical studies in hydrophobic systems catalyzed by polymeric imidazoles are limited to only a few instances.[16-20]

Recently, the authors have demonstrated that hydrophobic interaction in the ordered aggregate structures plays important roles in the enantioselective catalysis by optically active imidazole-containing polymers.[21] In the previous investigations we prepared the imidazole-containing copolymeric surfactants, poly (N-methacryloyl-L-histidine methyl ester (MHis)-co-N,N-dimethyl-N-hexadecyl-N-(11-methacryloyloxyundecanyl) ammonium bromide)s, and investigated that catalytic activity exhibited by those polymers toward the solvolyses of optically active activated esters, N-carbobenzoxy-D- and L-phenylalanine *p*-nitrophenyl esters (D-NBP and L-NBP). The copolymers which have large extended ordered aggregate morphology in the solvolytic solution showed remarkably enhanced enantioselective catalysis.

In the present investigation we have constructed another polymeric surfactant systems containing imidazole and benzene moieties in such a way that the systems were expected to form more rigid ordered structures when subjected to the solvolytic reactions than preceding system.[14,21] For the optically active imidazole-catalyst moiety, N-methacryloyl-L-histidine methyl ester (MHis) was prepared and copolymerized with surfactant comonomer, N,N-dimethyl-N-hexadecyl-N-[10-(*p*-methacryloyloxyphenoxycarbonyl)decyl] ammonium bromide (DEMAB). The copolymers of different monomeric ratios were prepared and the catalytic activities exhibited by those copolymers toward the solvolyses of optically active activated esters were examined in various conditions. And to look into the aggregate morphology of the copolymeric surfactants in the sonicated solvolytic solution, the turbidity and electron micrographs were observed.

Experimental

L-Histidine hydrochloride monohydrate, 11-bromoundecanoic acid, D-and L-phenylalanine, CDEAB were purchased from Aldrich Chemical Company and were used without further purification. Most of the organic compounds used in this study were reagent grade chemicals and further purified by distillation or recrystallization, when necessary. Some compounds were prepared by known procedures and spectral



Scheme 1

and physical data of the products were in accord with reported data. Methylene chloride and diethyl ether distilled over lithium aluminum hydride under nitrogen. Absolute ethanol was distilled under nitrogen from sodium metal. Pyridine was dried by distillation from KOH. Melting points were taken on a Thomas-Hoover melting point apparatus. All measured temperatures were uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 283 B Spectrophotometer. Proton NMR spectra were obtained on a Varian Model T-60 A and Varian FT 80-A Spectrometers, and chemical shifts are expressed in part per million from internal or external tetramethylsilane. Ultra-violet spectra were taken on a Shimadzu UV-200 Spectrophotometer. Merck silica gel 60(70-230 mesh) was used for column chromatography. Electron micrographs were taken on a JEOL JEM-100 CX electron microscope at Lucky Central Research Institute in Korea.

Syntheses of Substrates and Monomers. N-Carbobenzoxy-D- and L-phenylalanine *p*-nitrophenyl esters (D-NBP and L-NBP), N-carboethoxy-D- and L-phenylalanine *p*-nitrophenyl esters (D-NEP and L-NEP), D- and L-α-methoxyphenylacetic acid *p*-nitrophenyl esters (D-Man-PNP and L-Man-PNP), and MHis were prepared and purified according to the procedure described previously.[19,20,22,23]

N-N-Dimethyl-N-hexadecyl-N-[10-(*P*-methacryloyloxyphenoxycarbonyl)decyl]ammonium bromide (DEMAB) was prepared in the following manner (Scheme 1): To hydroquinone (5.00g, 45 mmol) and 1.19g (15 mmol) of pyridine in 50 m*l* of anhydrous ethyl ether were added 4.29 g (15 mmol) of 11-bromoundecanoyl chloride with stirring at 0 °C. After 1 hr the reaction mixture was washed with diluted HCl, aqueous sodium bicarbonate, and water. After solvent was removed, the crude product was introduced to petroleum ether in separatory funnel. The bottom layer was collected and crystallized from dioxane-water-acetonitrile. 2.10g (27% yield) of *p*-hydroxyphenyl 11-bromoundecanoate(**1**); m.p.

97-99 °C; ^{1}H NMR($CDCl_3$) δ = 6.80 (d, 4H), 5.61-5.40(br s, 1H), 3.50(t, 2H), 2.62(t, 2H), 2.30-1.40(br s, 16H). Methacryloyl chloride(0.76g, 7.2 mmol) was added to 2g(5.6 mmol) of **1** and 0.59g(7.2 mmol) of pyridine in 40 m*l* of anhydrous ethyl ether with stirring at 0 °C. After 1 hr the reaction mixture was washed with dilute HCl, aqueous sodium bicarbonate, and water. After solvent was removed, the oily product was placed on a silica gel column, and eluted with methylene chloride (Rf = 0.7). The combined fractions with same Rf value were evaporated. 1.5g(60% yield) of oily *p*-methacryloyloxyphenyl 11-bromoundecanoate (**2**). ^{1}H NMR($CDCl_3$ δ = 7.21(s, 4H), 6.45(s, 1H), 5.83(s, 1H), 3.50(t, 2H), 2.61(*t*, 2H), 2.10(s, 3H), 2.30-1.40(br s, 16H). 1.0g(2.35 mmol) of **2** and 0.70g(2.59 mmol) of N,N-dimethyl-N-hexadecylamine were heated for 2h at 65 °C. After cooling, the reaction product was crystallized from methylene chloride-n-pentane. 1.3g(75% yield) of DEMAB; m.p. 58-60 °C; ^{1}H NMR($CDCl_3$) δ = 7.21(s, 4H), 6.46(s, 1H), 5.86(s, 1H), 3.70(br m, 10H), 2.61(t, 2H), 2.10 (s, 3H), 2.31-1.41(br s, 47H);IR(KBr) 2935, 2910, 1695, 1600, 1460, 1234, 1047, 828 cm^{-1}.

Copolymerization. A representative copolymerization was as follows; MHis (2 mmol), DEMAB (2 mmol), and AIBN (1 mmol %) in dried ethanol were introduced into a polymerization tube. The solution was then degassed under vacuum and tube was sealed. After 48 h at 65 °C, the tube was opened and the content was added to a large volume of ethanol, and stirred for 30 min. The polymer was isolated on sintered glass funnel and dried in vacuum oven. Examination of the proton NMR spectrum revealed the complete disappearance of the vinyl and allyl protons. Yield; 36%, η_{inh} = 0.28 d*l*/g(1N HCl, 30 °C). From the copolymerization of MHis with DEMAB in various monomer feed ratios ([DEMAB]/[MHis]: 5, 10, and 20), we obtained the copolymers having imidazole-containing monomer (MHis) moiety of 14.7 mol %(P-a), 8.6 mol %(P-b), and 3.5 mol %(P-c) respectively. The stoichiometric compositions of the above copolymers were determined from their proton NMR spectra. But, investigation about the microstructure was not undertook.

Kinetic Measurement. Solvolytic rates were measured in the aqueous solution buffered with 0.02 M tris(hydroxymethyl) aminomethane and hydrochloric acid with sufficient potassium chloride to adjust the ionic strength to 0.02. In all cases, the solvolytic solutions were sonicated with Branson B-52 sonicator at 50 °C for 2h, and a 10-fold molar excess of catalyst over substrate was used. The reactions were followed by monitoring the concentration of released *p*-nitrophenolate ion at 400 nm with a Shimadzu UV-200 spectrophotometer. Kinetic data were treated as pseudo first-order by least square method ($r > 0.99$). The slope was corrected by subtracting the blank rate to obtain the observed rate constant k_{obsd}. The second-order rate constant k_{cat} was then calculated by dividing k_{obsd} by the catalyst concentration. Thus obtained k_{cat} values are to be called apparent catalytic constant. $k_{cat} = k_{obsd}$/[catalyst]

Electron Microscopy. The negatively stained samples were prepared as follows: To the solvolytic solutions (10 m*l*) of copoly(MHis-DEMAB) was added a 2% (w/w) aqueous solution (1 m*l*) of uranyl acetate. The aqueous sample was applied on a copper grid and the excess was blotted off. After being dried in a vacuum desiccator, the sample was introduced to a JEOL JEM-100 CX electron microscope.

Table 1. Apparent Catalytic Rate Constants[a] of Solvolyses of Optically Active D-NBP[b] and L-NBP by Copoly (MHis-DEMAB) in 0.02 mole / *l* Tris Buffer at 25 °C (pH 7.41)

Catalyst[c]	k_{cat}		k_{cat}(L-NBP)
	D-NBP	L-NBP	/ k_{cat}(D-NBP)
P-a	21.6	25.9	1.20
P-b	33.4	54.8	1.64
P-c	47.9	93.9	1.96

[a] k_{cat}: *l*/mole sec. [b] The concentration of the substrates: 1.07×10^{-5} mol/*l*. [c] The concentration of the catlysts: 1.00×10^{-4} mol/*l* (with regard to imidazole-containing residues).

Table 2. Apparent Catalytic Rate Constants[a] of Solvolyses of Optically Active D-NBP and L-NBP by P-c[b,c] in 0.02 mole / *l* Tris Buffer at pH 7.41

Temp. (°C)	k_{cat}		k_{cat}(L-NBP)
	D-NBP[d]	L-NBP	/ k_{cat}(D-NBP)
10	53.3	122.6	2.30
15	51.9	111.1	2.14
20	50.2	101.4	2.02
25	47.9	93.9	1.96
30	44.8	84.3	1.88

[a] k_{cat}: *l*/mole sec. [b] 3.5 mole % MHis and 96.5 mole % DEMAB RESIDUES. [c] The concentration of the catalysts: 1.00×10^{-4} mole/*l* (with regard to imidazole-containing residues). [d] The concentration of the substrates: 1.07×10^{-5} mole/*l*.

Results and Discussion

The solvolyses of optically active D-NBP and L-NBP by copolymers, poly(MHis-co-DEMAB) containing different amount of imidazole, were performed. Representative results are shown in Table 1.

The kinetic data in Table 1 show that all the copolymeric surfactants, poly(MHis-co-DEMAB), did exhibit much more enhanced catalytic activity than poly(MHis-co-dodecyl methacrylate) which can be characterized as hydrophobic random coils.[20] The increased reaction rate is certainly due to the higher local concentration of hydroxide ion attracted by the cationic surfactant of DEMAB in poly(MHis-co-DEMAB).[2] However, it should be noted that the enantioselectivity as well as the catalytic activity was also enhanced as the mol % of surfactant monomer DEMAB in the copolymer increased, indicating that hydrophobic interaction is operative in the mechanism depicted below[8] (E is the catalyst, S the substrate, (ES) the catalyst-substrate complex, (ES)' the intermediate acylate catalyst, and P is the leaving nitrophenolate ion.). It is conceivable that as hydrophobic interaction becomes more operative, the equilibrium concentration of (ES) will increase, exhibiting a higher solvolytic rate. The increase in equilibrium concentration of (ES) is due to the increased stability of (ES) in the surrounding tighter hydrophobic environment, thus exhibiting more ther-

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (ES) \xrightarrow{k_2} (ES)' + P$$

Table 3. Apparent Catalytic Rate Constants[a] of Solvolyses of Optically Active Substrate by P-c[b] in 0.02 mole / *l* Tris Buffer at 25°C (pH 7.41)

Substrates	k_{cat}		$\frac{k_{cat}(L)}{k_{cat}(D)}$
	D	L	
NEP[c]	35.8	38.7	1.08
Man-PNP[c]	24.6	26.1	1.06
NBP[e]	47.9	93.9	1.96

[a] k_{cat}: *l*/mole sec. [b] 3.5 mole % MHis and 96.5 mole % DEMAB residues. [c] N-Carboethoxy phenylalanine *p*-nitrophenyl ester. [d] *p*-Nitrophenyl α-methoxyphenylacetate. [e] N-Carbobenzoxy phenylalanine *p*-nitrophenyl ester.

modynamic enantiomeric preference in the (ES) formation.

Effect of Temperature. Hydrophobic interaction is known to be strongly temperature dependent[24] and it is of interest to observe the enantioselectivity in the presently investigated solvolytic reactions at different temperatures. Solvolytic reactions of D- and L-NBP were carried out with catalyst copolymer containing 3.5 mol% of MHis at different temperature and the results are summarized in Table 2.

As shown in Table 2 the reaction rate changed abnormally and increased rather than decreased as the temperature was lowered, and the enantioselectivity was also enhanced as the reaction rate increased. These results also indicate that hydrophobic interaction is operative in the rate determining complex-formation step as in the mechanism discussed above, *i.e.*, the surrounding environment becomes more hydrophobic at lower temperatures, and thus the stability of (ES) will increase. These phenomena are well in accord with the previous observations.[19,20]

Effects of Substrate Structures. Since in the catalytic mechanism are generally involved the complexation of the catalyst with the substrate and the catalyst-substrate complex is apolar in character, the influence of hydrophoic interaction upon catalysis can be important. Overberger *et al.*[8-10] have demonstrated the significance of such hydrophobic interactions in catalysis by imidazole-containing polymers. To further confirm the possible role of hydrophobic interaction in the present enantioselective solvolytic systems, the activated esters of different alkyl sizes such as D- and L-NEP, NBP, and Man-PNP were used as substrates. The results of solvolyses of these optically active substrates by copolymer containing 3.5 mol % of MHis are shown in Table 3.

The values in Table 3 show that in the case of solvolyses of D- and L-NEP and Man-PNP, there is no significant difference between the catalytic rate constants for the solvolyses of two enantiomeric substrates. When the more hydrophobic substrates, D- and L-NBP, were used, the polymeric imidazoles exhibited not only enhanced catalytic activity but also observable degree of enantioselectivity. The difference in solvolytic rates of D- and L-NBP was clear with preference for L-enantiomer. This difference may be attributable to the increased hydrophobicity of the system and also to the presence of aromatic group in the structure of substrate D- and L-NBP. In the comparative examination of kinetic data of the solvolyses of D- and L-NBP and Man-PNP, it seems that the hydrophobic aromatic group attached to the asymmetric center of phenylalanine plays an important role in the preferential hydrophobic interaction between L-enantiomers of polymeric catalyst and substrate.

Table 4. Apparent Catalytic Rate Constants[a] for the Solvolyses of D- and L-NBP by the Polymeric Imidazoles in the Aggregate System of P-c[b] and Micellar Surfactant at pH 7.41

Micellar Surfactant[c]	k_{cat}		$\frac{k_{cat}(L\text{-NBP})}{k_{cat}(D\text{-NBP})}$
	D-NBP	L-NBP	
Triton X-100	2.6	2.9	1.10
SDS[d]	13.6	14.7	1.08
CDEAB[e]	47.8	112.3	2.35

[a] k_{cat}: *l*/mole sec. [b] 3.5 mole % MHis and 96.5 mole % DEMAB residues. [c] 60 mole % P-c and 40 mole % micellar surfactant. [d] Sodium dodecyl sulfate. [e] Cetyldimethylethylammonium bromide.

Table 5. Apparent Catalytic Rate Constants[a] of Solvolyses of Optically Active D- and L-NBP in the Coaggregate System of P-c[b] and CDEAB[c] at 25°C (pH 7.41)

Catalyst[d]	k_{cat}		$\frac{k_{cat}(L\text{-NBP})}{k_{cat}(D\text{-NBP})}$
	D-NBP	L-NBP	
90	31.7	76.4	2.41
70	31.1	88.7	2.85
50	43.4	108.6	2.50
30	49.7	115.7	2.33
10	62.5	126.3	2.02

[a] k_{cat}: *l*/mole sec. [b] 3.5 mole % MHis and 96.5 mole % DEMAB residues. [c] Cetyldimethylethylammonium bromide. [d] The numbers below mean the mole % of CDEAB in the coaggregate system, which are derived from ([CDEAB]/([CDEAB]+[DEMAB moiety in copolymer])) × 100.

Effect of Micellar Surfactants. There have been abundant experimental evidences indicating that micellar effects are operative in stereoselective chemical reactions.[25-30] Brown and Bunton[25] investigated enantioselective micelle-promoted hydrolyses of optically active esters by micelle-forming histidine derivatives and proposed a possible strong interamide hydrogen bonding as the main cause for the enantioselectivity. Meanwhile, Ueoka *et al.*[6] have recently reported the significant microenvironmental effect of cationic rod-shaped coaggregates formed with a vesicular surfactant and a micellar surfactant on the enantioselective cleavage of amino acid *p*-nitrophenyl esters as catalyzed by histidine-containing tripeptides. Thus, in order to see the effect of micellar surfactants on our polymeric systems the coaggregate systems of copolymer P-c and micellar surfactants such as nonionic Triton X-100, cationic cetyldimethylethylammonium bromide (CDEAB), and anionic sodium dodecyl sulfate (SDS), were prepared and introduced to the solvolyses of optically active esters. The results are shown in Table 4.

The values in Table 4 show that the catalytic activity was rather reduced in the coaggregate systems of copolymer P-c with Triton x-100 and SDS compared with that of copolymer P-c. However, in case of the coaggregate system of copolymer P-c and cationic CDEAB the activity was enhanced. In the case of coaggregates of copolymer P-c with Triton x-100 and SDS any enantioselectivity was not observed and it seems that in the above two cases the micellar surfactants disturb the aggegates of the polymeric cationic surfactant

Table 6. Turbidities of Solvolytic Solutions Measured from Absorbance A at 400 nm

Catalyst	P-a	P-b	P-c
Absorbance A	0.358	0.477	0.648

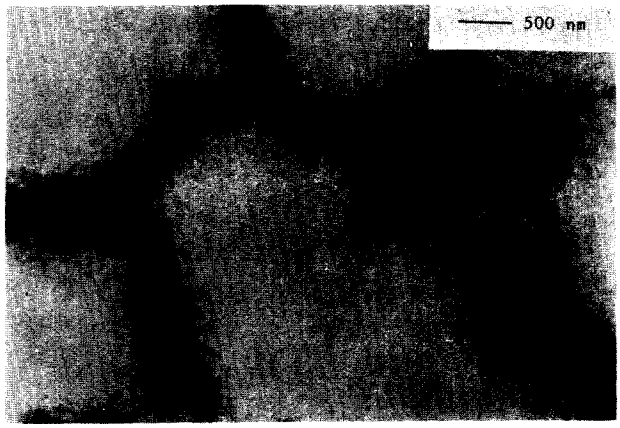


Figure 2. Electron micrograph for the aggregates of copoly(MHis-DEMAB); negatively stained with 2.0 wt% uranyl acetate; Tris buffer (pH 7.41) solution sonicated with Branson B-52 sonicator at 50 °C for 2 h.

P-c rather than give the tighter ordered coaggregates. However, it is to be noted that in the case of coaggregates of P-c with CDEAB the enantioselectivity is also increased.

To observe the miximum enantioselectivity, the coaggregate systems of P-c and CDEAB were prepared by varying the composition of P-c and CDEAB and subjected to the catalytic solvolyses of D- and L-NBP. The results are summarized in Table 5.

As shown in Table 5 the maximum enantioselective catalysis, *viz.*, $k_{cat}(L)/k_{cat}(D) = 2.85$, was observed in case of composition of 70 mol% of CDEAB and 30 mol% of MHis moiety. Thus it seems that the two surfactants in solvolytic solution at this composition take efficient morphological structures for preferential hydrophobic interaction on L-enantiomer pairs.[6]

Aggregate Morphology of Copoly (MHis-DEMAB). To investigate the aggregate morphology of P-c in the sonicated solvolytic solution, the turbidity and electron micrographs were taken .The turbidity measured from absorbance at 400 nm of the solvolytic solutions at pH 7.41 are shown in Table 6.

The data in Table 6 show that the turbidity of sonicated solvolytic solutions of copoly (NHis-DEMAB) were all large and increased in proportaion to the decrease of mol% of imidazole-containing monomer in the copolymer. From the observation of the relation between turbidity and vesicular size in aqueous solution,[31] it was supposed that all the solvolytic solutions employed have large extended aggregates of copolymers.

The electron micrograph of the aggregate of P-c in solvolytic solution is shown in Figure 2. The electron micrograph shows that the solvolytic system employed has large extended aggregated with the diameter of 100-500 nm, which appears to be large multilayered vesicles. And this result is consistent with the observation of the change in turbidity of the solvolytic solution. Although the certain ordered aggregate structures were also seen with other copolymers in solvolytic solutions on the electron micrographs, the formation of the above structures was not clear. From those results, it seems to suggest that hydrophobic interaction in ordered aggregate structure plays an important role in the enantioselective catalysis of optically active imidazole-containing polymers.

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The Crystal and Molecular Structure of Cholesteryl Isobutyrate

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The structure of cholesteryl isobutyrate, $(CH_3)_2CHCOOC_{27}H_{45}$, was determined by single crystal X-ray diffraction methods. Cholesteryl isobutyrate crystallized monoclinic space group $P2_1$, with a = 15.115 (8)Å, b = 9.636 (5)Å, c = 20.224 (9)Å, β = 93.15 (5)°, z = 4, Dc = 1.03 g/cm^3 and Dm = 1.04 g/cm^3. The intensity data were measured for the 3417 reflections, within $\sin\theta/\lambda = 0.59$Å^{-1}, using an automatic four-circle diffractometer and graphite monochromated Mo-K_α radiation. The structure was solved by fragment search Patterson methods and direct methods and refined by full-matrix least-squares methods. The final R factor was 0.129 for 2984 observed reflections. The two symmetry-independent molecules (A) and (B) are almost fully extended. The molecules are in antiparallel array forming monolayers with thickness d_{100} = 15.2Å, and molecular long axes are nearly parallel to the [$\bar{1}$01] directions. The two distinct molecules form separate stacks with almost the same orientations, but with differing degrees of steroid overlap. Thers is a close packing of cholesteryl groups within the monolayers. The packing type is similar to those of cholesteryl hexanoate and cholesteryl oleate.

Introduction

Cholesterol[1-3] which is the most abundant steroid in the animal kingdom, and is found mainly as a component in cell membranes and lipoproteins. In addition to being a primary metabolic precursor for many of the steroid hormones, it and some of its esters play an important role in the structural stabilization of membranes[4]. Thus an important first step towards deriving detailed structural models of membranes is a study of the stereochemistry and packing of cholesterols and its derivatives. Although cholesterol first attracted the interest of X-ray crystallographers[2] more than four decades ago, it is only recently that the detailed crystal structures of cholesterol and some of cholesterol derivatives have been determined. The reason for this delay is undoubtedly the complexity of the crystal structures, arising from a consistent tendency of cholesterol to crystallize with more than one independent molecules in the crystallographic asymmetric unit. Another remarkable feature of these cholesterol structures is the presence of local pseudo-symmetry, that is, noncrystallographic symmetry which is satisfied locally, to remarkably high degree. In addition to the complexity and the pseudo-symmetry, an object of interest is the characteristic bilayer nature of the structure of cholesterol crystals, with a molecular arrangement generally similar to that of cholesterol in biological membranes[5].

Barnard and Lydon have conducted a crystallographic study on fourteen straight chain cholesteryl esters[6]. Examination of their unit cell parameters in addition to other crystallographic data, suggests that majority of esters may have one of the three common crystal packing arrangements. These arrangements differ with respect to the portion of the ester molecules that are involved in intermolecular interactions and therefore determine the crystal structure. These structure types differ according to the relative importance of three kinds of molecular interactions, namely cholesteryl-cholesteryl (Type II Monolayer)[7-12], cholesteryl-fatty acid (Type I Monolayer)[13] and fatty acid-fatty acid (Bilayers)[14].

The crystal structure analysis of the cholesteryl isobutyrate is one of a series of cholesteryl ester structure determinations which we have undertaken. From consideration of the crystal data of the cholesteryl isobutyrate, it seemes interesting to study its crystal structure, because the different mode of crystal packing type tends to be present in this compound.

Experimental

Cholesteryl isobutyrate from Tokyo Kasei Kogyo Company Ltd. was recrystallized by slow evaporation of an ace-