Studies of Helical Aggregates of Molecules. III. The Bivalent Metal Soaps of Optically Active 12-Hydroxyoctadecanoic Acid

Taro TACHIBANA, Kazuko KAYAMA, and Hideko TAKENO

Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo

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The bivalent metal soaps of optically-active 12-hydroxyoctadecanoic acid were found to crystallize out in the form of twisted fibers from aqueous or anhydrous ethanol solutions. Most soaps of this class produced both right-handed and left-handed fibers from the same specimen, more of the latter in the case of the D-enantiomer. An enantiomorphic relationship of the sense of twist was clearly demonstrated by using both enantiomers of the Ca soap. Under a high-resolution electron microscope, it was observed on the Sr soap that Sr atoms are arranged in lines along the fiber axis with a periodicity of 33—40 Å, showing that the hydroxyoctadecanoate chains of the soap molecules are aligned approximately parallel to the width of the fiber. The twisting of the soap fibers was associated with the layer structure characteristic of soap.

The present work represents an extension of previous studies[1,2] of the sense of twist of helical aggregates of optically active 12-hydroxyoctadecanoic acid and its alkali metal soaps. Some bivalent metal soaps also have been found to form twisted fibers.[3] However, since it had been seen that some soaps of this class, *e.g.*, the Mg soap, produce the right-handed fibers only on some occasions and the left-handed fibers only on other occasions, it was difficult to draw definite conclusions as to the sense of twist of these soap fibers from a small number of experiments. Therefore, experiments have been carried out repeatedly under various conditions.

Generally, the bivalent metal soaps are liable to decompose and release their free acid with a rise in the temperature. For this reason, the crystalline aggregates were allowed to separate out from the C_2—C_8 fatty alcohols into which the soaps are to some extent dissolved without decomposition at temperatures below 100°C. Some soaps thus produced fibrous aggregates, while other soaps, such as the Sr, Ni, and Pb soaps, separated out, in the most part, as amorphous aggregates. Fortunately, we have found that the latter soaps also produced well-developed and twisted fibers when separated out from an alcohol solution containing water. Thus, for the bivalent metal soaps also, it became possible to obtain reliable information about the sense of twist of the soap fibers.

Experimental

The purification of D-12-hydroxyoctadecanoic acid (hereafter abbreviated as "D-acid") from a commercial product has been described previously.[1] The bivalent metal soaps of this acid were prepared by methathesis, at 50°C in aqueous ethanol, between the Na soap and chlorides or sulfates of the corresponding metals. The soaps thus obtained were washed with distilled water, then with ethanol, and finally with acetone, and well dried over P_2O_5 at room temperature. Gravimetric analysis demonstrated that the soaps, which are listed in Table 1, were all the disoaps with the formula of $Me(C_{18}H_{36}O_3)_2$. The water of crystallization was measured by thermogravimetry. The X-ray diffraction patterns, the infrared absorption spectra, and the differential thermographs were also investigated.

To obtain the soap fibers, the soap sample was dispersed into an alcoholic solvent under ultrasonic irradiation and then heated on a water bath. After the excess has been filtered off, the hot solution were allowed to cool to room temperature with stirring. Thus, the Ca and Cd soaps gelled at room temperature, while the other soaps separated out as flocculates or precipitates from the solution. The samples of the Hg and Mn soaps, which are susceptible to thermal decomposition, were carefully treated at a temperature lower than 50°C.

In certain cases, the soap fibers were produced by neutralizing the D-acid in a hydrocarbon solvent, Nujol, with an aqueous solution of the hydroxide of the corresponding metal at a certain high temperature and by then allowing the hot solution to cool to room temperature with stirring. The Nujol solution became grease at room temperature. It was confirmed by infrared analysis that the grease contained no free acid. On the other hand, when the grease was obtained by cooling the Nujol solution in which the soap samples had previously been dissolved at a high temperature (100—160°C), it was demonstrated by infrared analysis that a part of the soap samples was decomposed and free acid was released.

The procedure for observing the aggregates by means of an electron microscope was described in a previous paper.[1]

Results and Discussion

1) Characteristics of the Bivalent Metal Soaps. Since no data on the bivalent metal soaps of 12-hydroxyoctadecanoic acid have yet been described in the literature, some of them are given, together with the data for stearate soaps reported by Matsuura[4] in Table 1. One can see some characteristics of the hydroxyoctadecanoate soaps by comparing them with the stearate soaps.

i) Water of crystallization: With regard to the water of crystallization the hydroxyoctadecanoate soaps are similar to the corresponding stearate soaps.

ii) The infrared absorption spectra: Two infrared absorption bands are found at about 1400 cm^{-1} and 1550 cm^{-1}, they are due to the symmetric and asymmetric stretching vibrations respectively of the carbox-

1) T. Tachibana and H. Kambara, This Bulletin, **42**, 3422 (1969).

2) T. Tachibana, S. Kitazawa, and H. Takeno, *ibid*, **43**, 2418 (1970).

3) T. Tachibana and H. Kambara, *J. Colloid Interfac. Sci.*, **28**, 173 (1968).

4) R. Matsuura, *Nippon Kagaku Zasshi*, **86**, 560 (1965).

TABLE 1. CHARACTERISTICS OF D-12-HYDROXYOCTADECANOATE SOAPS, $Me(C_{18}H_{36}O_3)_2 \cdot xH_2O$
ν=infrared absorption peak for asymmetric vibration of COO^-
d=X-ray long spacing

Me	Mg	Ca	Sr	Ba	Mn	Ni	Cu	Zn	Cd	Hg	Pb
	2	1	0	0	1	1	0	0	0.5	1	0.5
x	(2 & 3	1	0	0	1	2	0	0	0	0	0)[a]
ν (cm^{-1})	1570	1573	1550	1563	1565	1565 sh	1590	1550	1563 sh	1585	1562 sh
											1550
	broad	1533	1538	1520	1545	1550		1538	1550	1565	1525 sh
											1510 sh
										1540 sh	1503
	49.7	50.3	50.2	49.4	49.8	50.5	47.8	46.5	49.6	48.3	50.3
d (Å)	(49.3	49.8	48.1	47.5	47.7	48.8	47.6	42.6	50.2	50.0	50.8)[b]
	or 52.9										

a), b) Numerical values in parentheses represent those for the corresponding soaps of stearic acid.[4]

ylate ion. Matsuura[4] pointed out that the latter band is broadened or split into two or more bands in the hydrated stearate soaps. However, this splitting of the band was observed for all of the hydroxyoctadecanoate soaps used here, whether hydrated or not.

iii) The X-ray diffraction patterns: The hydroxyoctadecanoate soaps show a long spacing of around 49 Å, this is almost the same value as that of the corresponding stearate soaps, as is shown in Table 1. This value corresponds approximately to double the length of the hydroxyoctadecanoate chain, meaning that the hydroxyoctadecanoate soaps have a layer structure such as that established in the crystal structure of fatty acid and its soaps. It is also common to both the hydroxyoctadecanoate and stearate soaps that the Zn soap gives an abnormally low value of long spacing. It can also be pointed out that the hydrated soaps generally show higher values in the long spacing than do the unhydrated soaps.

The short spacing, which is associated with the interchain distance, is generally broader in the hydroxyoctadecanoate soaps than in the corresponding stearate soaps. The Mn, Ni, and Cu hydroxyoctadecanoates exhibited a diffraction pattern composed of diffuse bands, thus indicating low crystallinity. Here these results will not be taken into consideration further; the present paper will deal mainly with the sense of twist of the soap fibers.

2) The Form of the Aggregates. It was found that the bivalent-metal soaps of the D- (or L-) acid do not always form fibrous aggregates, but produce twisted fibers under appropriate conditions.

Typical electron micrographs are presented in Figs. 1 and 2. These photographs were made to show the same direction as that of the twist of the specimen.

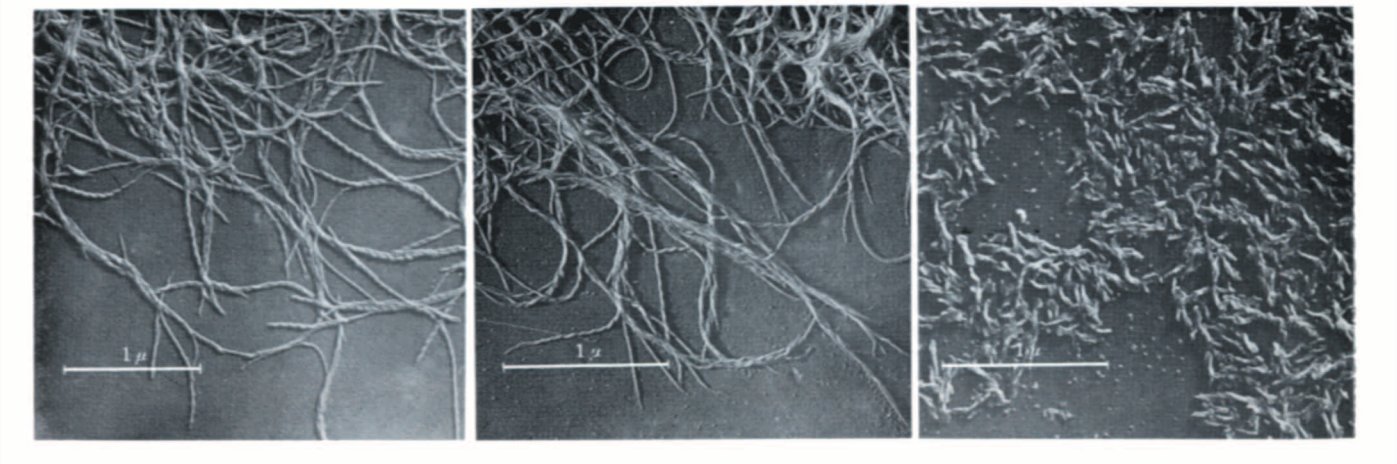
The size and form of the fibrous aggregates and their sense of twist were characteristic of the individual soap under certain conditions. For example, when separated out from ethanol, the Mg soaps produced fibers of a reasonably uniform width of 0.03 μ, while the Sr, Mn, Cu, Cd, Hg, and Pb soaps often produced two types of fibers at the same time: (i) thin fibers of about 0.03 μ wide, with a small pitch of twist, and (ii) ribbons of large dimensions and with a large pitch of twist. The Zn soap precipitated from ethanol in a form of platelets, with a trace of twisted fibers (right-handed and left-handed fibers). This fact may be associated, in some manner, with the abnormally low value of the X-ray long spacing of this soap.

The bivalent metal soaps often produced both right-handed and left-handed fibers at the same time in ethanol. Which type of twisted fibers was more abundant, depended on the solvent used. The Ca soap (D-form) alone exhibited a behavior different from the other soaps in that it produced exclusively the right-handed fibers, not only from alcohols, but also from Nujol. In this connection, the Ca soap showed the same behavior as the Li soap.

3) Enantiomorphic Relationship for the Helical Sense. The relationship between the two enantiomers was previously established for the fibers of the free D- (or L-) acid and of its alkali metal soaps[1] and for the fibers of synthetic polypeptides.[5] As the same relationship can also be expected for the bivalent metal soaps, it was examined by the use of the Ca soap. The fibers from the Ca soap of the D-acid showed a right-handed twist, while those from that of the L-acid showed a left-handed twist, regardless of the solvent used. The Ca soap of the DL-acid (racemic form) gave amorphous precipitates. These micrographs are shown in Figs. 1a, b, and c. Thus it was also demonstrated, for the Ca soap, that the sense of twist in the helical aggregates is primarily associated with the optical isomerism. However, other bivalent metal soaps of the one enantiomer often produced both right-handed and left-handed fibers from the same solution. The same phenomenon was previously observed with the Na and K soaps.[1] This shows that some factors obscure the effect due to the asymmetry of molecule.

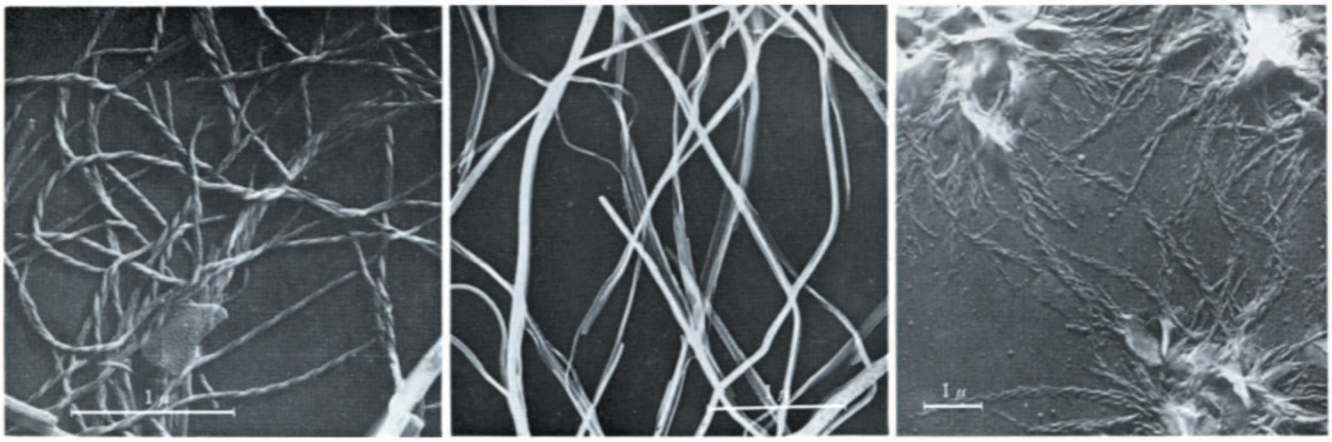
4) Solvent Effect on the Sense of Twist. Solvent effects have already been reported for the fibers of the free D- (or L-) acid and of its Li soap, the twist of which showed a one-handed sense in the C_2—C_4 alcohols

5) T. Tachibana and H. Kambara, *Kolloid-Z. Z. Polym.*, **219**, 40 (1967); this paper reports that enantiomorphism is found between helical aggregates of the D-isomer and the L-isomer of poly-γ-benzyl glutamate. Thereafter, we have found the same result with poly-γ-methyl (ethyl, *n*-propyl, or *i*-propyl) glutamate. These polypeptides also gave right-handed fibers for the D-enantiomer and left-handed fibers for the L-enantiomer.



a) D-form, right-handed twist. b) L-form, left-handed twist. c) DL-form, no twist.

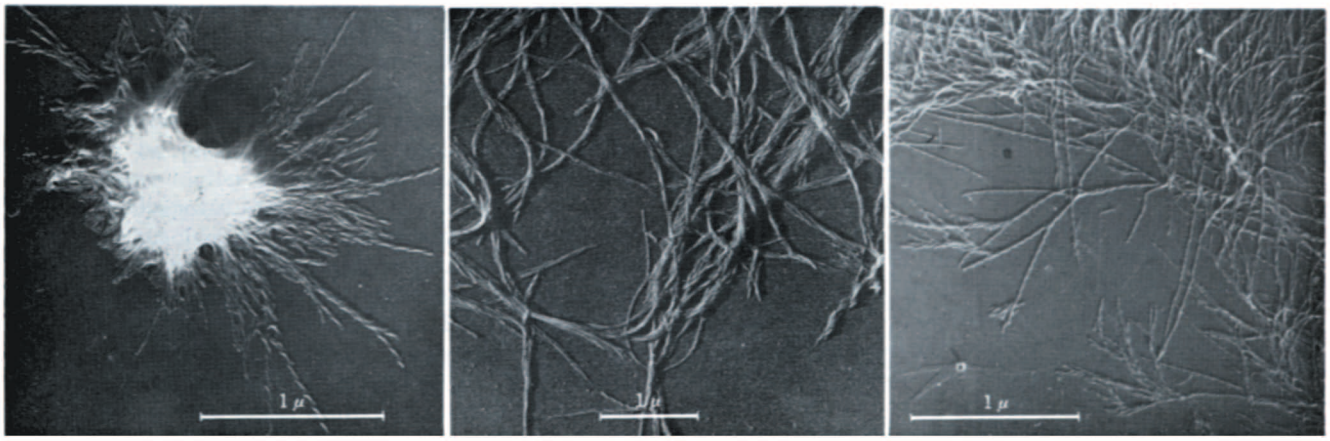
Fig. 1. Enantiomorphic relationship in helical aggregates of Ca 12-hydroxyoctadecanoate.



a) Sr soap from aqueous ethanol, fresh precipitate, left-handed twist.

b) Sr soap from aqueous ethanol, aged precipitate, no twist.

c) Ba soap from ethanol, left-handed twist.

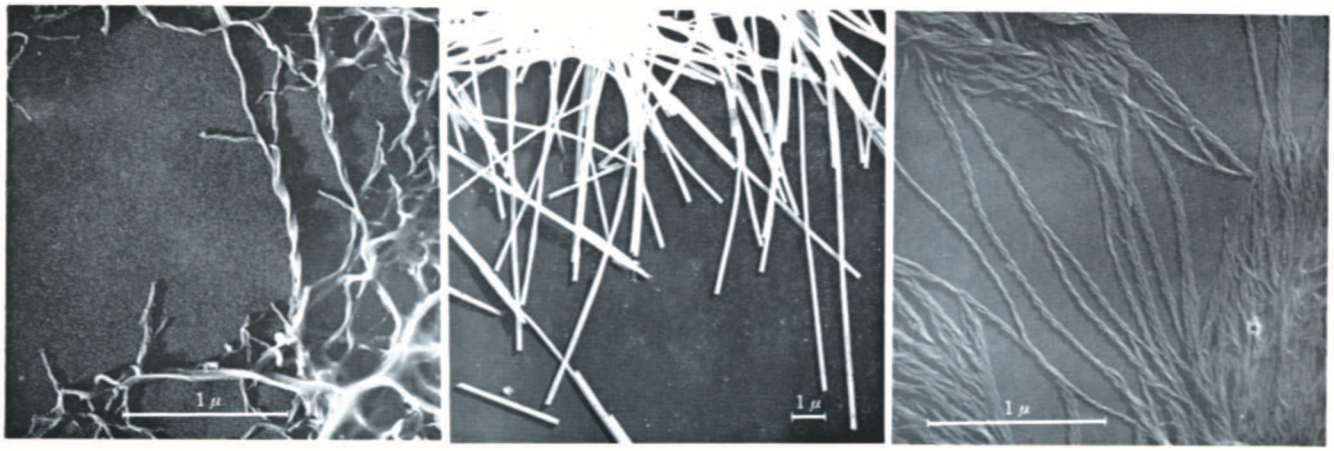


d) Mg sorp from ethanol, left-handed twist.

e) Mn soap from ethanol, left-handed twist.

f) Ni soap from aqueous ethanol, left-handed twist.

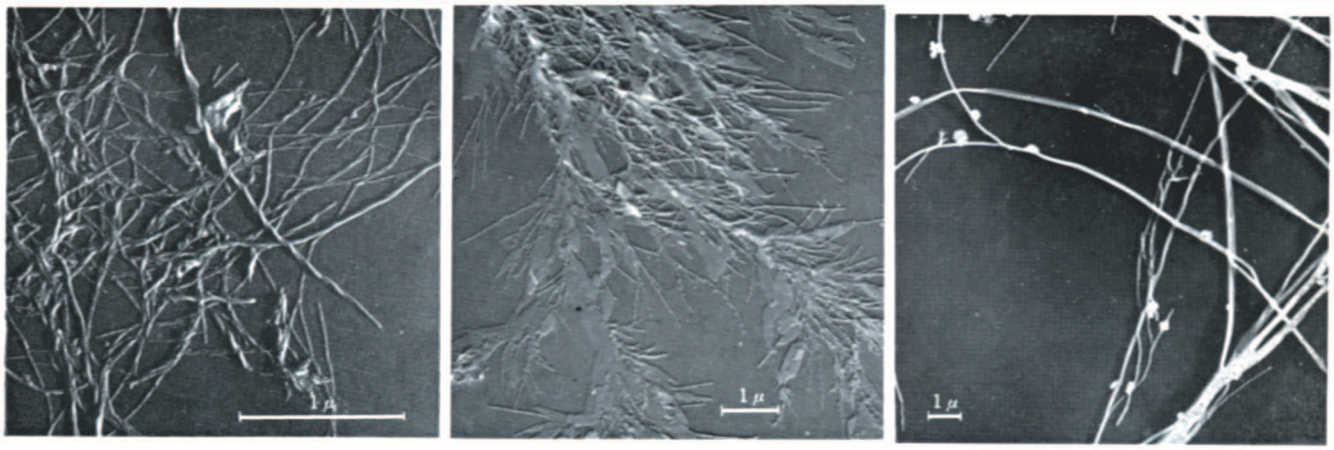
Fig. 2. Twisted fibers of bivalent metal soaps of D-12-hydroxyoctadecanoic acid.



g) Cu soap from ethanol, right-handed and left-handed twists.

h) Zn soap from aqueous ethanol, no twist.

i) Cd soap from aqueous ethanol, left-handed twist.



j) Cd soap from Nujol, right-handed twist.

k) Hg soap from ethanol, left-handed twist.

l) Pb soap from aqueous ethanol, left-handed twist.

Fig. 2. Twisted fibers of bivalent metal soaps of D-12-hydroxyoctadecanoic acid (continued).

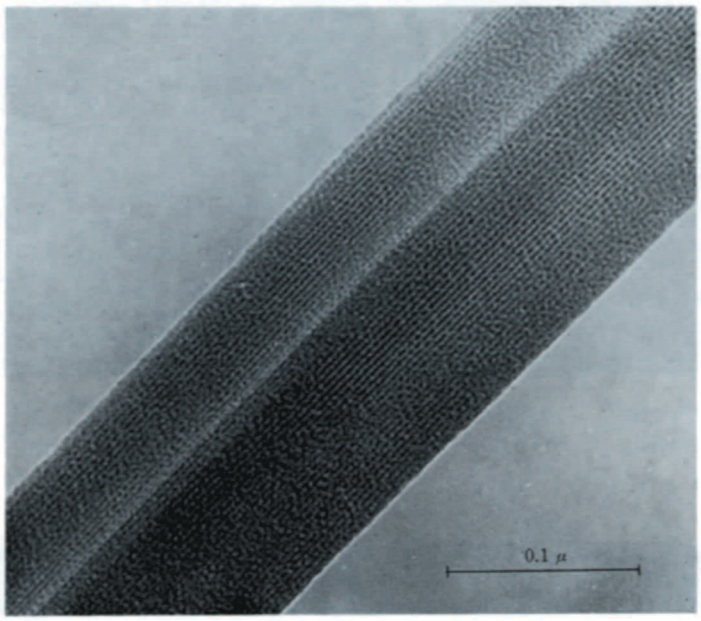


Fig. 3. Sr soap fiber from aqueous ethanol, showing structural detail at high resolution.

and both senses in longer alkyl chain alcohols. For the Mg and Cd soaps also, an effect was found similar to that observed with the Li soap. The Mg soap of the D-acid produced predominantly the left-handed fibers from alcohols, while produced predominantly the right-handed fibers from Nujol. On the other hand, the Cd soap produced both right-handed and left-handed fibers from alcohols at the same time, though the fraction of the right-handed fibers increased with the length of the alkyl chain in a series of normal fatty alcohols, and right-handed fibers were exclusively produced from Nujol. It is interesting to note that, with regard to the sense of twist, polar or hydroxy solvents such as alcohols have effects contrary to those of such non-polar solvent as Nujol. This is not due to a difference in the crystalline phase between the soap crystal from alcohols and that from Nujol, since the samples from both solvents gave the same X-ray diffraction patterns. Accordingly, the solvent effect observed here can be regarded as a result of a crystal habit. Probably the polar-nonpolar structure of the soap crystal is associated with the observed effect. The possibility of a solvent effect due to an optically active solvent such as optically active amyl alcohol, was examined in the Ca soap, but no effect was observed.

5) The effect of Water. It was found that the presence of water in alcohols greatly influences the form of the soap aggregates. The Ca soap produced the twisted fibers from anhydrous ethanol, as is shown in Fig. la, but it produced only platelets from aqueous ethanol. However, the Sr, Ni, and Pb soaps, which were precipitated mostly as amorphous aggregates from anhydrous alcohols, produced a large number of twisted fibers from aqueous ethanol containing 5%(v/v) water (Figs. 2a, f, and 1). These fibers developed greatly with an increase in the water content, so that the sense of twist was more clearly observed with such fibers. However, the Pb soap from aqueous ethanol gave wider and larger ribbons, in which the twist was little observed. On the other hand, the Zn, Ba, and Cd soaps showed little effect of water on the form of the soap aggregates. An infrared spectral examination showed that the Ca, Sr, and Ba soaps recovered from aqueous ethanol were hydrated salts.

The water effect was observed also when the soaps were crystallized out from Nujol. For example, the Mg, Sr, and Ba soaps yielded fibers twisted a little from Nujol containing no water, but well-developed fibers were obtained when the metal soaps were prepared by neutralizing the D-acid in Nujol with an aqueous solution of the corresponding bivalent metal salts or when soaps previously prepared were dissolved into Nujol containing a certain amount of water at a high temperature. In these experiments, it was necessary to choose the most appropriate temperature.

Previously, Birdsall *et al.*[6] observed in a commercial Ca tallowate-minral oil grease, that the soap fibers were present only when a sufficient amount of water had been incorporated into the grease from which the fibers are formed. In this case, the soap crystallized out was of a hydrated form. These results evidently indicate that water in alcohols or Nujol plays some role in developing the soap crystal as a fibrous form. However, in the case of the hydroxyoctadecanoate soaps, the anhydrous soaps also produced the twisted fibers, as has already been described. Therefore, the twisting is not specific to the hydrated soap. Probably water aids in the development of soap fibers during the crystal growth.

6) Aging Effect. It was observed that the soap fibers changed their form when allowed to stand in the solution from which the fibers had been produced; the Cu soap gave left-handed thin fibers and right-handed wide ribbons immediately after it was separated out from ethanol, but the right-handed ribbons were found predominantly in the aged precipitate; the Ni soap produced a globular aggregates as the initial precipitate, and left-handed fibers from the aged precipitate.

The presence of water in ethanol was found to promote the change of the form of the aggregate; the Sr soap produced left-handed thin fibers and non-twisted ribbons as the initial precipitate, and non-twisted wider ribbons alone after sufficient aging (see Figs. 2a and b); the Pb soap initially produced left-handed fibers, and ribbons after aging. These changes were accelerated by increasing the water content in ethanol.

The Ca and Cd soaps often yielded such large twisted fibers that they were visible under an optical microscope. Such fibers were prepared by crystallizing these soaps out from aqueous ethanol and by then evaporating the solvent very slowly. The sense of twist for the large fibers was the same as that in the thin fibers previously observed by means of an electron microscope.

Table 2. The sense of twist in the fibers from bivalent metal soaps of D-12-hydroxy-octadecanoic acid

Soap	The sense of twist solvent		
	ethanol	aqueous ethanol	Nujol
Mg	l	l	r & (l)
Ca	r	platelet	r
Sr	(l)	l	(r) & (l)
Ba	(l)	platelet	(r) & l
Mn	r & l		
Ni	(l)	(r) & l	
Cu	r & l	(r) & l	
Zn	(r) & (l)	(r) & l	
Cd	r & l	(r) & l	r
Hg	r & l	l	
Pb	(r) & (l)	l	

r: right-handed twist; l: left-handed twist.
(r) or (l) means the presence of a trace of the corresponding twist.

6) D. H. Birdsall and B. B. Farrington, *J. Phys. & Colloid Chem.*, **52**, 1415 (1948).

7) General Remarks on the Sense of Twist. The sense of twist of the soap fibers is summarized in Table 2. From this table, one can see a tendency for the bivalent metal soaps of the D-hydroxyoctadecanoate to favor, more or less, the formation of the left-handed fibers. The same tendency has also been found for all the alkali metal soaps except for the Li soap. This is considered to be a reflection of molecular asymmetry in the sense of twist of the soap fibers. However, it is characteristic of the bivalent metal soaps that both types of twisted fibers are, except in the case of the Ca soap, produced from the same specimen, although which type is predominant depends on the solvent used.

8) Fine Structure of Fibers. The observation of the structure of soap fibers by high-resolution electron microscopy was made using the Sr soap, which is comparably heat-resistant. The specimens were prepared by allowing a drop of the aqueous ethanol solution to dry on a micro-plastic grid for electron microscopy. The micrographs were photographed at an instrumental magnification of 100,000 X in a JEM-100B electron microscope without further treatment. Twisted thin fibers (width, 0.01 μ) and comparably large ribbons (width, about 0.1 μ) were found; the fine structure could be observed in the latter. Figure 3 shows a typical micrograph, in which striations are seen running parallel to the lengths of the fibers. The spacing of these striations is 33—40 Å, which approximates to the long spacing value of 47.5 Å derived from the X-ray diffraction patterns of the soap. Taking into account the uncertainty of the instrumental magnification, this indicates that Sr atoms all arranged in lines along the fiber axis with a periodicity of about 40 Å, and that the hydroxyoctadecanoate chains of the soap molecules all aligned approximately parallel to the width of the fibers. This is in accord with the observations on Na laurate fibers made by Camp and Shuttleworth[7] and on Ca soap fibers made by Bird and Rooney.[8]

The thickness of the ribbon was too thin to be estimated, probably being less than 50 Å. We observed a considerable disordered part where the striations were not seen on the surfaces of the ribbon; the ribbon consisted of a crystalline region and an amorphous region. From such a fine structure, it is presumed that each surface of a ribbon involves polar groups and non-polar alkyl chains of the hydroxyoctadecanoate molecules, and that the thin sides of it consist of polar groups alone or of non-polar groups alone, depending upon the polarity of the solvent from which the ribbons have been separated. One might expect that such thin ribbons would tend to twist themselves or to associate with one another as the result of the free energy requirement. In fact, the electron micrographs demonstrate that the structure is made up of two or more individual fibers twisted about one another. A similar structure is also encountered in twisted fibers of optically non-active soaps such as Na myristate and Ca tallowate. In these cases, both right-handed and left-handed fibers were observed. On the other hand, it has been established by the X-ray diffraction study that the crystal structure of long chain fatty acid and its salt is composed of alternately ionic layers and hydrocarbon layers, stacked on one another. These facts suggest that the twisting of the soap fibers results from the layer structure characteristic of soap. The one-handed twist of thin fibers composed of optically-active molecules is due to the asymmetry of the fiber structure itself.

In this series of studies, an enantiomorphic relationship in helical aggregates has been clearly demonstrated for 12-hydroxyoctadecanoic acid and its Li and Ca soaps. Other soaps of this acid produced both right-handed and left-handed fibers from the one enantiomer and, then, one of them was more or less predominant: the fibers from the univalent and bivalent metal soaps of the D-acid are inclined to twist to the left. This result is evidence that the sense of twist in the macrohelix is determined by the molecular asymmetry. Since biological fibers often exhibit a one-handed twist, it may be suggested that, in this case also, molecular asymmetry may play a role in determining the sense of twist at any stage of the fiber formation.

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7) M. Camp and T. H. Shuttleworth, *Nature*, **183**, 535 (1959).
8) R. J. Bird and G. Rooney, *ibid.*, **190**, 337 (1961).