Variations in Crystal Structure Within Certain Isologous Series of Long-Chain Compounds. A Review of Some Basic Features[1]

FOR THE PURPOSES of this paper "long-chain compounds" are defined as those whose molecules are comprised, for the greater part, of polymethylene chains of about 10 carbons or more. As Vand (16) has said, "long-chain compounds exist in a bewildering number of polymorphic forms." Efforts at classification of these forms have been successful in varying degrees according to whether there was maintained sufficient regard for basic differences without over-emphasis of detail. Quite naturally the greatest success in classification of polymorphs occurred with homologous series, and there exists a number of sets of unrelated nomenclatures for different series. However it appears possible to classify most polymorphic forms of long-chain compounds into a limited number of structure types, especially if such polar compounds as soaps and sulfonates are excluded.

There is, of course, for long-chain compounds, a similarity in liquid states which show a limited degree of order characterized by sufficient chain alignment to give diffuse 4.6 Å spacings corresponding to chain separation. (More polar compounds, such as soaps, fatty acids, and alcohols, in contrast to the less polar paraffins and triglycerides, have shown long-spacings which are greater than the chain length but considerably less than twice that length.)

Detailed crystal structure study and assignment of space groups from single-crystal patterns has been very limited in comparison with the extensive study of crystal powder patterns. Accordingly present classifications of the crystal-structure type must be based on the latter.

Müller (11) has put forth for hydrocarbons, and Lutton (8) has adapted to glycerides, the proposal of three main types of cross-sectional structure which seems to apply to the vast majority of solids comprised of long-chain molecules which are not highly polar. Malkin's objections (10) to such a proposal, on the one hand, attribute to it too great a degree of pretentiousness and, on the other, minimize the fact that the strongest short-spacings are substantially independent of the long-spacings; when similar and classifiable for different compounds, these short-spacings must arise from geometries of crystal cross-section which are likewise similar and classifiable.

For want of better terms, these cross-sectional types are here designated *alpha, beta prime,* and *beta* as in the previous proposal for glycerides (8). They may be defined and described as follows.

Alpha. This term has been commonly used to refer to crystalline states of low density and high translucence. They characteristically permit little or no supercooling. Alpha-type forms may be stable or metastable; if stable, they are the highest melting forms. On an x-ray diffraction pattern there is a single strong short-spacing of about 4.2 Å. This type of pattern is universally interpreted to mean that the long-chain axes of the parallel polymethylene chains (viewed end-on) are arranged in perfect hexagonal array. It is commonly assumed that the chains are rotating or are in random orientation about these axes. Most, but perhaps not all, *alpha* forms are perpendicular, *i.e.,* have their chain axes perpendicular to the plane of the end methyl groups.

Beta Prime. The more dense, more opaque *beta prime*-type forms may or may not permit supercooling. They may be stable or metastable. The associated strong short-spacings are about 4.2 and 3.8 Å, but many weaker lines may appear. On the basis of single-crystal study, especially on fatty acids, such forms are presumed to have cross-sectional structures in which projections of odd rows of zigzag chains show the same (or nearly the same) orientation while even rows show another orientation. This type of cross-section is perhaps the most general. It is common to the variety of 3-dimensional structures dealt with by Schoon (14) in an interesting proposal to systematize long-chain polymorphism.

Beta. These forms, like those of the *beta prime* type, are more dense and more opaque than *alpha,* may be stable or metastable, and may or may not permit supercooling. They are characterized by a strong, usually strongest, 4.6 Å short-spacing but have many other lines as well. The zigzags of all chains are assumed to be identically (or nearly identically) oriented as has been suggested for the triclinic *beta* form of trilaurin (15). *Beta*-type forms are usually if not always tilted.

A particular polymorph of a long-chain compound is assumed to belong to a given cross-sectional type when its short spacings conform approximately to the values given for that type. As a consequence, designation of the phase type in this paper will not necessarily conform to usage in the literature. It is not to be expected that such a system of classification will hold with perfect generality or that minor variations are not numerous where it does hold. Nevertheless it has been useful with triglycerides, for instance. Among the mixed C_{16}–C_{18} triglycerides, in contrast with tristearin which shows all three cross-sectional types, 2-stearoyl dipalmitin shows only *alpha* and *beta prime* while 2-palmitoyl distearin shows only *alpha* and *beta* (6).

It was thought that an interesting application of the cross-sectional classification could be made to the two isologous series: (I) methyl palmitate (P), ethylene glycol dipalmitate (PP), glycerol tripalmitate (PPP), and m-erythritol tetrapalmitate (PPPP), and (II) the corresponding stearates S, SS, SSS, and SSSS.

Experimental

Of the eight compounds intercompared, both x-ray and m.p. data have been reported for four, the two methyl esters (9, 2) and the two triglycerides (8).

PP was prepared by direct esterification of 50 g. of palmitic acid (setting point 62.0°) with 5 g. ethylene glycol (Baker's purified) in the presence of 0.9 g. of p-toluene sulfonic acid. Recrystallization from acetone gave 23 g. of a product with complete m.p. of 70.2° [Lit. 68.7° (12)] and saponification no. 208.1 (theory 207.9).

SS was prepared by alcoholysis from 50 g. of methyl stearate (m.p. 40°) with 5 g. of ethylene glycol in the presence of 0.35 g. of NaOMe suspended in xylene. Recrystallization from acetone gave 31 g. with a complete m.p. of 77.0° [Lit. 75° (12)] and saponification no. 186.5 (theory 188.5).

PPPP was prepared by reaction of 88.4 g. palmitoyl chloride (setting point of acid 62.0°) and 6.1 g. of m-erythritol (Eastman) in pyridine solution for 4½ hrs. at 120–125°. The crude mix was poured over ice, taken up in hexane, and washed with dilute HCl and H_2O. Crystallization and washing with hexane removed most of the deep red color. Two crystallizations from benzene yielded 36.0 g. with complete m.p. 83.6° and saponification no. 209 (theory 208.6). An infrared curve indicated the absence of OH groups but showed the expected correspondence with saturated triglyceride.

SSSS was prepared by direct esterification of 50 g. of stearic acid (setting point 69.0°) with 4.88 g. of m-erythritol (Aldrich) in the presence of 1.2 g. of p-toluene sulfonic acid and 0.9 g. of sulfuric acid. Nine hours of refluxing in 50 cc. of xylene yielded 2.9 cc. H_2O. The crude product was neutralized and washed in hexane solution with 50–50 ethanol-H_2O and with NaCl-brine, then crystallized in hexane to give a top ⅓ melting at 82°. Three crystallizations from benzene yielded 7.6 g. of complete m.p. 87.5° and saponification no. 188.5 (theory 188.8). An infrared curve indicated absence of OH groups and showed the expected correspondence with saturated triglyceride.

Phase behavior of the glycol and m-erythritol esters was studied by x-ray and m.p. techniques previously described (6). Flat-film patterns were obtained with a G. E. XRD unit. Sample-to-film distance was 5.0 or 10.0 cm. Rapid and regular complete m.p.s were obtained after appropriate sample treatment. Only a single m.p. range was observed for each of the four esters. Results are reported in Tables I and II.

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TABLE I

Comparison of P, PP, PPP, and PPPP

	P (9)	PP	PPP(8)	PPPP
Complete M.P. (°C.)	29.6(10)	70.2	66.4	83.6
No. of M.P.s	1	1	3	1
X-ray data (Å)				
Alpha	....	....	45.6 4.14 VS	....
Beta prime				
L.S.	43.5	41.9	42.3	41.0
S.S.	(4.05 S,[a] 3.69 S)[b]	4.12 VS, 3.68 S	4.28 VS, 3.78 S	4.31 S–, 4.11 S, 3.83 S–
Beta				
L.S.	......	......	40.6	38.8
S.S.	......	......	5.24 M, 4.61 VS, 3.84 S, 3.68 S	5.44 M, 4.59 S, 4.07 M 3.87 M+, 3.77 S

[a] VS—very strong, S—strong, M—medium.

[b] Probably same as for methyl stearate.

Discussion

Isologous Series of Palmitates and Stearates. The palmitic and stearic isologous series of Tables I and II are very similar except for the lack of an *alpha* form in PPPP. There is an interesting alternation of m.p.s, involving a very sharp rise from the methyl ester with a dip at the triglyceride. This dip and the relatively great stability of metastable triglyceride forms bespeak some difficulty in fitting into the stable form's lattice.

Of the two lower members of a given series, *e.g.,* S and SS, each has but a single form which is of *beta prime* type. Mixtures of P and S give *alpha* forms (2). SSS exhibits *alpha, beta prime,* and *beta* forms, each stable enough for m.p. determination. SSSS shows all three forms. Its *alpha* form is fleeting and transforms without visible evidence of melting to *beta prime* in 5 sec. at 50°C. As has been said, PPPP shows no *alpha. Beta prime* forms of both PPPP and SSSS are stable for 5 sec. at 80°C. but in one day at 60°C. transform, substantially in the case of SSSS and completely in the case of PPPP, to stable *beta* forms.

It would be of interest to study the polymorphism of the tetrastearate of dl-erythritol. That there would be important differences from the present data for m-erythritol esters is suggested by the following:

Compound	M.P. °C.(3)
m-erythritol	122
m-erythritol tetraacetate	89
dl-erythritol	72
dl-erythritol tetraacetate	53

Alpha Tendency of Long-Chain Compounds. The two series which have just been discussed represent but a small number of the long-chain compounds whose x-ray diffraction behavior has been studied. It is interesting to survey the field broadly in relation to the proposed cross-sectional types.

It soon becomes evident that certain types of molecules are *alpha*-formers while others are not. It is not always easy to draw sharp lines. Some members of a homologous series may form *alpha,* like SSSS, and others, like PPPP, may not. Some form *alpha* in mixture but not when pure. A reasonably accurate if not complete listing of types of compounds, some of whose pure members form *alpha,* is as follows: paraffins (13), triglycerides (8), 1,2-diglycerides (4), 1-monoglycerides (8), ethyl esters (13), m-erythritol tetraesters (13), acetates (13), formates (13), alcohols (5), iodides (13), and ketones (13). Non-*alpha* formers are fatty acids (13), soaps (1), 1,3-diglycerides (8), 2-monoglycerides (8), methyl esters (9), fatty acid anhydrides (9), and glycol diesters.

Many types of molecules permit the *alpha* structure. Asymmetry (as in 1- *vs.* 2-monoglycerides), low polarity (as in paraffins *vs.* soaps), mixture (as in mixed methyl esters *vs.* pure esters) and high molecular weight (as in SSSS *vs.* PPPP) favor *alpha.* It is probable that other factors are quite important, such as branching and sizes of groups incorporated in the chains.

There is reason to believe that the 1-monoglyceride *alpha* forms are tilted (7) for their long spacings are too short for a doubled molecular length. This unusual feature among *alpha* forms must arise from the large glyceryl moiety. (The similar moiety in 2-monoglycerides also contributes to short long-spacing, but there is no *alpha* form.)

Beta Prime and Beta Tendency of Long-Chain Compounds. Triglycerides and paraffins, as classes of compounds, are notable formers of all three cross-sectional types. SSSS forms all three; PPPP forms both *beta prime* and *beta.* Palmitic and stearic acids exhibit two *beta prime* types of form, metastable B and stable C, and one *beta* type of form, metastable A (9).

Among compounds which do not form the very common *beta prime* type, most notable are the 1,3-diglycerides (8) which show two *beta* types. The *beta*-tending triglyceride, 2-palmitoyldistearin, has already been mentioned.

Among compounds showing *beta prime* but not the *beta* type are alcohols (5), methyl and ethyl esters (13), and glycol diesters, also the aforementioned triglyceride, 2-stearoyldipalmitin. Insertion of a –CHOH group in the middle of the molecule changes the *beta prime*-tending glycol ester into the *beta*-tending 1,3-diglyceride.

It seems likely that rather small influences are responsible for directing a compound toward one cross-sectional type or the other; moreover almost equal *beta prime* and *beta* tendencies are possible, as in the case of the triglyceride 1-palmitoyl distearin (8).

Summary

Crystal structures of many long-chain compounds appear classifiable into *alpha, beta prime,* or *beta* cross-sectional types, in which, respectively, the rows of parallel chains have axes randomly oriented, identically oriented within a row but with orientation alternating among the rows, or identically oriented throughout. Members of two isologous series are compared with particular regard to the cross-sectional type. The series are (I) methyl palmitate (P), ethylene

TABLE II

Comparison of S, SS, SSS, and SSSS

	S(9)	SS	SSS(8)	SSSS
Complete M.P. (°C.)	38.25(10)	77.0	73.1	87.5
No. of M.P.s	1	1	3	1
X-ray data (Å)				
Alpha				
L.S	......	......	50.6	51.2
S.S	......	......	4.14 VS	4.13 S
Beta prime				
L.S	48.0	41.9	46.8	45.5
S.S	4.05 S, 3.69 S	4.12 VS, 3.68 S	4.18 VS, 3.78 S	4.30 M, 4.11 S, 3.81 M+
Beta				
L.S	......	......	45.15	42.8
S.S	......	......	5.24 M, 4.61 VS, 3.84 S, 3.68	5.38 M−, 4.55 S, 4.01 W+, 3.86 M, 3.72 S−

glycol dipalmitate (PP), glycerol tripalmitate (PPP), and m-erythritol tetrapalmitate (PPPP); and (II) the corresponding stearates. The following behavior is observed—P: *beta prime;* PP: *beta prime;* PPP: *alpha, beta prime, beta;* PPPP: *beta prime, beta;* and similarly for the stearate series but with an additional *alpha* form for SSSS. Other compounds are considered with respect to tendency to form various cross-sectional types.

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Announces Judges for Fatty Acid Award Mss.

THE THREE JUDGES of the fourth annual competition for the $500 Fatty Acid Award given by the Fatty Acid Producers Council of the Association of American Soap and Glycerine Producers Inc. for the best manuscript on fatty acid chemistry will be B. M. Craig, Prairie Regional Laboratory, National Research Council, Saskatoon, Saskatchewan; R. T. Milner, Department of Food Technology, University of Illinois, Urbana; and C. F. Raschke, Conway Oil Company, Denison, Tex.

Deadline for the competition is July 15, and announcement of the winner(s) will be made during the fall meeting of the American Oil Chemists' Society at the Hotel Sherman, Chicago, October 20-22.

The award is administered by the Society, through a special committee headed by C. W. Hoerr, Armour and Company, Chicago, and is given for work done in an educational institution in the United States or Canada while the individual is a candidate for a degree or on the staff of an educational institution within one year after receipt of such a degree.

Submission of a paper or thesis may take place within one year after the author is graduated. In respect to team authorship, at least one of the candidates must meet the requirements as set forth, in which event the entire team shall be considered eligible for the award.