Review of the Polymorphism of Saturated Even Glycerides[1]

E. S. LUTTON, Chemical Division, The Procter and Gamble Company, Cincinnati, Ohio

ASIDE from its direct bearing on the technologically important matter of fat crystallization, the polymorphism of glycerides is of interest because of its increasing application to the study of fat composition. The quantity of information recently published on the subject without any comprehensive critical review and the confusion that has developed in the literature due to differing points of view suggest that it is time to attempt a clarification. If glyceride polymorphism seems complicated to those who desire merely a speaking acquaintance, this is unfortunate for in major features it is simple and is nicely related to the polymorphism of other long chain compounds.

The phenomena of glyceride polymorphism have long been recognized in terms of the "double-melting" effect of fats formerly attributed by many to isomerism. It is remarkable that Duffy (1) showed correctly as early as 1852 that tristearin has three melting points. His work went long unnoticed and the triple melting of tristearin was rediscovered by Othmer (2) in 1915. It remained for Malkin and associates (3) to demonstrate conclusively that the basis for this multiple melting was actually polymorphism, i.e. occurrence, for a given compound, of different crystalline forms distinguishable by x-ray diffraction pattern. Three other groups of workers (4, 5, 6) independently came to the conclusion that Malkin was partially in error in his association of melting points with diffraction patterns. Out of the differences in such associations has arisen most of the confusion that exists in the literature. Unfortunately neither side in the matter has significantly changed position so that the confusion may continue for a time. Recent reviews (7, 8), whether favoring one school or the other, have arrived at untenable compromises of the two viewpoints which are definitely not reconcilable with respect to the major points of difference. The present account is written entirely from the point of view of the later mentioned observers (4, 5, 6). [This is a modification of the provisional position taken in an earlier more extensive review (9).]

Long Chain Crystallization

Long chain compounds of paraffinic type (e.g. paraffinic hydrocarbons, fatty acids, and triglycerides) show a number of common features in their crystallization behavior.

The long zig-zag paraffin chains crystallize with long axes parallel; the resulting cross-sectional arrangements (which give rise to the so-called short spacings) are few in number for relatively non-polar molecules such as the glycerides. The most important of these arrangements are illustrated in later discussion specifically concerned with glycerides.

Molecular end groups, whether they be methyl or polar groups, associate with each other to form planes so that certain repeat distances (long spacings) in the long chain crystal correspond to integral multiples of the molecule (or chain) length. In many cases tilting of long chain axes with respect to end group planes shortens the observed long crystal spacing. The fitting of zig-zags in successive chains, when tilting occurs, is indicated schematically (for hexane) in Figure 1.

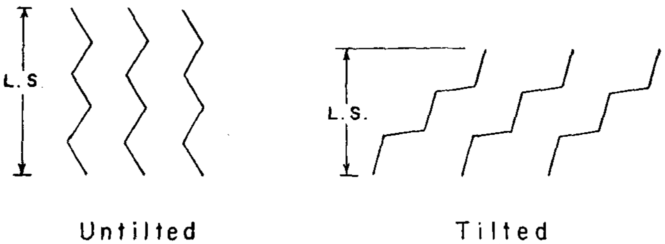

FIG. 1. Basis for tilting (hexane).

It is the polarity and geometry of the molecule which determine whether the long spacing corresponds to a single or to multiple chain lengths as is shown for triglycerides in the next section.

Glyceride Crystallization

Glycerides, despite considerable molecular complexity, are in some respects rather typical long chain compounds. This is particularly true of the cross-sectional arrangements for triglycerides.

Nomenclature

It is these cross-sectional arrangements which give the primary basis for nomenclature of polymorphic forms (4) through the associated short spacings. This basis for nomenclature is illustrated in Table I.

TABLE I

Basis of Nomenclature for Glyceride Forms

Form	Short Spacing Pattern Characteristics
Alpha	A single strong line corresponding to approximately 4.15 Å.
Beta Prime	Usually two (but occasionally more) strong lines corresponding to approximately 4.2 and 3.8 Å.
Beta	A strong (usually strongest) line corresponding to approximately 4.6 Å.

Cross-Sectional Structure

The cross-sectional arrangements (of the chains, not the molecules) presumed to be associated with these structures are indicated in Figure 2. These are the same arrangements that have been proposed for hydrocarbons by Müller (10). In Figure 2 the black circles represent the chain axes. The main short spacings to which the arrangements give rise are indicated in the drawing.

The alpha type of cross-section is hexagonal. It is just the arrangement obtained on grasping tightly a number of rods of equal diameter. The chains either rotate or are in random orientation about their axes. Alpha is a low density structure whose cross-section is about 20 Å^2 per chain. It almost universally involves untilted or perpendicular chains. If realized at all for a given material (glyceride or other long

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chain compound), it is the first form obtained on chilling the melt.

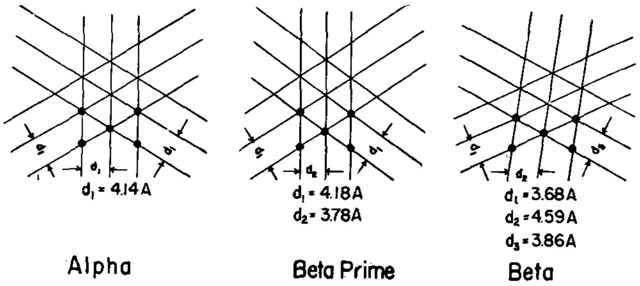

FIG. 2. Cross-sectional structures.

The beta prime type structure is clearly the most common for long chain compounds. It is the type discussed in Schoon's enlightening article (11) on crystalline long chain compounds. Among glycerides this structure type is generally associated with tilted chains, but perpendicular "beta prime-like" structures are observed for some long chain compounds; and reversible "alpha" to "perpendicular beta prime" transformations are common, e.g. among hydrocarbons.

The beta structure, although relatively uncommon among long chain compounds, is well nigh universal for triglycerides. It is normally the stable form and is almost invariably associated with tilted chains. Both beta prime and beta are more dense in cross-section than alpha, each chain cross-section occupying about 18.5 Å^2.

Each of the three structure types is presumed to be subject to minor modification without fundamental architectural change. Most saturated triglycerides show all three cross-sectional structure types and no others. Unsaturated triglycerides tend to show differences from typical behavior. Greater differences appear for mono- and diglycerides.

Chain Length Multiplicity

The geometry of triglycerides and their possible variations in geometry from compound to compound give rise to major variations in crystal structure in the long chain direction. A triglyceride long spacing may include one, two, three, or four segments not necessarily of equal lengths but in general corresponding with the lengths of constituent fatty acid chains. The number of segments is here called "the chain length multiplicity"; the structure types thought to be associated with recognized "multiplicities" are illustrated in Figure 3 (without regard to tilting of chains). The common type of structure for saturated glycerides is a double structure with reversed tuning forks (handles beside prongs) forming an essential part of the repeated structural unit. If chain lengths in a given structure differ by four or more carbons, triple structures (12) may appear, where short chains have sorted from long chains by a slipping of the reversed tuning forks until they are handle beside handle to effect better "space filling." In the case of unsymmetrical glycerides tuning fork arrangements may give way to triple-chain-length "chair-type arrangements" as indicated in Figure 4. Substantial chain length difference may also give rise to quadruple-chain-length structures which seem to be essentially doubled double structures. (Thus far these have been encountered only in association with beta prime cross-sections.) If a very great difference in chain length exists, so-called single-chain-length structures (13) can occur.

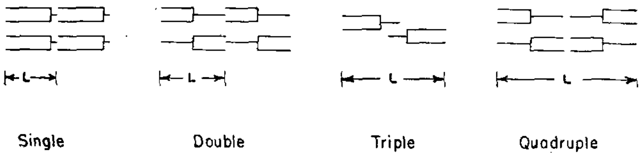

FIG. 3. Chain length multiplicity.

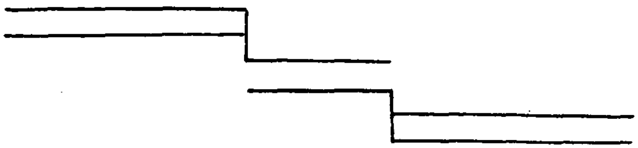

FIG. 4. Unsymmetrical or "chair" arrangement.

Chains of Unequal Length

While chain length difference does give rise to frequent departure from double-chain-length structure, the powers of accommodation of double structure for chains of unequal length is considerable. The evidence is that in such cases of "accommodation" those chains which extend beyond their shorter neighbors "crumple up" sufficiently to fill substantially the otherwise void parts of the structure. Observations leading to similar conclusions have been made on solid solutions of soaps (14, 15).

To designate a form of alpha cross-section and double-chain-length structure the term "alpha-2" is used, and similarly "beta-3" for triple-chain-length beta structures. The simple designation "beta" generally refers to the more common double-chain-length structure.

Lowest Melting Form of Triglycerides

As has been indicated, much of the confusion in the literature on triglyceride polymorphism arises from differences of opinion as to the nature of the lowest melting form of tristearin for instance. Clarkson and Malkin (3, 16) have called this form a glass. That the form is not a glass in the usual sense (17) is clear from the following properties which it shows:

a) Sharp melting point.
b) Anisotropy.
c) Sharp diffraction lines not in the position of the typical diffuse lines of liquid fat.
d) Large difference in viscosity from melt (manifested within a few degrees).
e) Discontinuity in specific volume on melting.
f) Discontinuity in heat content on melting.

The real problem however is not whether a form, which is actually crystalline is called a glass, but rather what properties, including x-ray diffraction lines, are truly associated with the lowest melting point. This review is written with the point of view that the lowest melting form of tristearin is crystalline (or closely approaches a crystalline state in degree of organization); that it definitely has a long spacing value of about 50 Å; that it is properly called alpha in analogy with forms of other long chain compounds, so-named; and that no glassy forms (with 4.2 Å short spacing but without long spacings) exist.

Further difficulties arise from this question as to whether a glassy form exists. Acceptance of such a phase means, with alpha, beta prime, and beta patterns in addition to deal with, that four phases with presumably four different melting points exist, no reversible solid-solid transformations having been reported for triglycerides. The three melting levels found characteristic of tristearin by several observers (1, 2, 18, 19, 3, 4, 5) had to be increased to four by Clarkson and Malkin (16) when they observed a beta prime pattern for tristearin, long familiar to them in the case of mixed glycerides (20) but not reported in earlier work (3) on tristearin. The position taken in the present review is that tristearin, tripalmitin, etc. (and many mixed glycerides) have no more than three characteristic melting levels; these are, as a rule, the lowest, next, and highest of Malkin's four levels.

Variations of Melting Point

Malkin and associates have supported their claims of four melting points by thermal curve and melting point techniques. Breaks or peaks in thermal curves can be misleading if not clearly established after variation in rates of cooling and heating. As for melting points, it is relatively easy to establish lowest and highest melting levels for glycerides, but intermediate levels encounter the complication that a given form of a given glyceride can show significant spread in melting level, as much as 3°C., according to degree of "stabilization" of the form. It is presumed that this stabilization involves change in crystallite size and in crystallite perfection. Evidence in the polymer field is conclusive that long chains can be better or worse aligned according to the history of the sample.

Polymorphism of Tristearin and Its Homologues

Tristearin can be considered the type compound for triglyceride polymorphism. Its three distinct melting points at 54, 64, and 73°C. are associated respectively with alpha, beta prime, and beta x-ray patterns, illustrated schematically in Figure 5. The alpha form is invariably obtained in any moderately rapid cooling. Beta prime and beta are capable of marked supercooling, but cooling only slightly below the alpha m.p. instantly starts alpha crystallization. Alpha is stable for weeks at room temprature. Near its melting point it transforms rapidly to beta prime. Beta prime is best obtained (free of beta) by crystallization from the melt a little above the alpha m.p. There is no record of the form being obtained from solvent in the case of tristearin. Beta prime goes rapidly to beta near its m.p. Beta is obtained directly from melt only very slowly; it is readily obtained from solvent. A substantially pure beta will vary in melting point (by "thrust in" technique) by as much as 3°C. according to degree of stabilization.

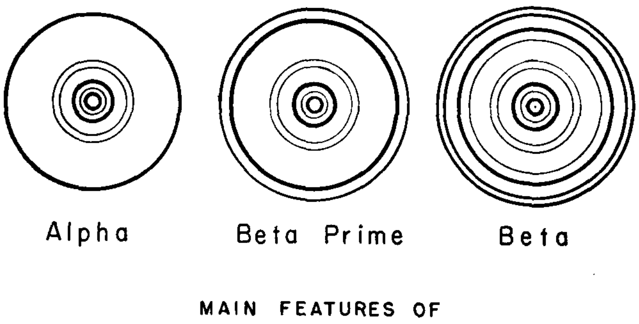

FIG. 5. Triglyceride diffraction patterns.

TABLE II

Melting Points and Long Spacings of Tristearin and Homologues C_{10} through C_{18} (3, 5)

Carbons in Fatty Acid Chain	M.P.'s °C.			Long Spacings (Å)		
	Alpha	Beta Prime	Beta	Alpha	Beta Prime	Beta
10	–15	18.0	31.5	......	......	26.8
12	15	35.0	46.4	35.6	32.85	31.2
14	33	46.5	57.0	41.2	37.65	35.8
16	44.7	56.6	66.4	45.6	42.3	40.6
18	54	64	73.1	50.6	46.8	45.15

In Table II appear m.p. and long spacing data for tristearin and homologues. In Figure 6 is depicted the thermal behavior of a small sample of tristearin treated in a manner to manifest its three forms. The cooling curve, Figure 6a, shows alpha crystallizing from the melt, then proceeding to beta prime, which in turn goes to beta. If alpha or beta prime is prepared and brought to the corresponding melting point by being subjected to an environment just slightly above that m.p., sudden heat evolution, due to transformation to the next higher form, is observed as shown in Figures 6b and 6c. The melting of beta is shown in 6d.

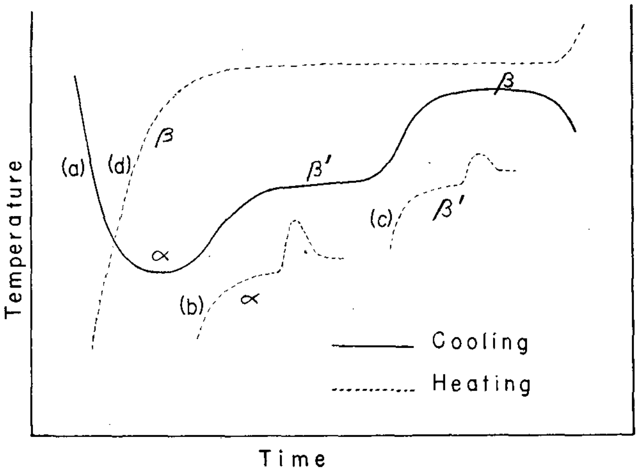

FIG. 6. Schematic thermal curves for tristearin.

By microscopic observation (21) it is found that on direct crystallization from the melt alpha gives small spherulites with individual crystallites generally indistinguishable; beta prime gives larger spherulites sometimes with individually distinguishable crystallites showing parallel extinction; beta gives crude spherulites or blades having non-parallel extinction. The anisotropy of the form obtained on chilling the melt (namely alpha) is perhaps the most conclusive evidence possible that it is not a "glass."

The homologues of tristearin such as tripalmitin do not differ significantly in general principles of behavior. Corresponding melting points are lower and transformation rates are faster as chain length is decreased.

It is of interest that odd triglycerides, such as trimargarin, have been found by Clarkson and Malkin (3) to show the usual type of m.p. alteration between odd and even members of the series.

Heats of fusion have been determined on two forms of tristearin (22). Alpha gives a value of 38.9 cal./

gm. and beta 54.5 cal./gm. It would be presumed that the beta prime value is intermediate.

Studies of the specific volume of tristearin, etc. lead to the values 0.988 for beta and 1.027 for alpha at 30°C. [see experimental curve, Figure 6, of the reference cited (23)].

Polymorphism of Saturated C_{16}-C_{18} Mixed Triglycerides

The saturated C_{16}-C_{18} mixed triglycerides are of importance for including among their number the major components of most highly hydrogenated vegetable oils. While their behavior is in many respects reminiscent of that of tristearin and tripalmitin, there are differences indicated in Table III which serve as a basis for sharp distinction (24).

TABLE III

Melting Points and Long Spacings of Palmitic-Stearic (P-S) Triglycerides (24)

Glyceride	Melting Points °C.			Long Spacings (Å)		
	Alpha	Beta Prime	Beta	Alpha	Beta Prime	Beta
SSS	54.9	64	73.1	50.6	46.8	45.15
SPS	51.8	......	68.5	49.2	......	43.1
PSS	50.6	61.1-65.0*	65.2	48.5	45.1	44.7
PSP	46.5	68.6	......	46.65	42.75	......
SPP	47.4	57.7-61.7*	62.7	47.6	43.8	42.1
PPP	44.7	56.6	66.4	46.8	42.3	40.9

* According to degree of stabilization.

These mixed glycerides, like tristearin, all exhibit a lowest melting alpha form—unusually stable in the case of SPS, unusually labile in the case of PSP. Occurrence of forms other than alpha can be briefly tabulated (Table IV).

TABLE IV

Forms of Mixed Palmitic-Stearic Glycerides

Glyceride	Forms Beside Alpha
SPS	Only beta (or extremely fleeting beta prime).
PSP	Only beta prime.
PSS	Only beta prime from melt, beta from solvent (beta prime and beta equally stable).
SPP	Beta prime and beta (beta stable).

Other Mixed Saturated Triglycerides

In this review no attempt is made to cover in detail the diverse behavior of other mixed triglycerides. It has been mentioned that new structure types are apt to arise as chain length difference exceeds two. Variations with molecular structure and polymorphic form are so numerous as to require quite detailed discussion in any thorough consideration of these compounds. It should be pointed out however that the number of polymorphic forms may increase with increasing chain length difference. Thus for 1-stearyldilaurin (SLL) four forms have been found (12): alpha-2, beta prime-2, beta prime-3, and beta-3; and also for 2-myristyldistearin (SMS) (25): alpha-2, beta prime-2, beta prime-4, and beta-3. The *number* of forms is in agreement with Malkin's conclusions, but it must be realized that the four diffraction patterns do not include the proposed vitreous pattern of Malkin; and beta prime-3 is additional for SLL, beta prime-4 for SMS.

A very limited amount of work has been done on saturated triacid triglycerides (26), and it suggests that these glycerides, while having their own individuality, resemble related diacid triglycerides in polymorphic behavior.

Unsaturated Triglycerides by Comparison

Unsaturated compounds are appropriately discussed under the present title only by way of comparison. Triunsaturated, e.g. triolein (27), trielaidin, and mixed elaidic-stearic (or palmitic) triglycerides (28) give double-chain-length structures. Mixed oleic-saturated glycerides show considerable tendency toward triple structure formation (6, 29, 28) especially in the case of stable forms. This involves a segregation of saturated from unsaturated chains comparable to the short from long chain segregation observed with many mixed saturated triglycerides. See Figure 7.

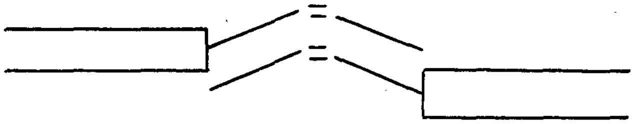

FIG. 7. Disaturated arrangement.

1,3-Diglycerides

The 1,3-diglycerides according to Baur *et al.* (30) show two forms called beta-a and beta-b for the series dilaurin through distearin. It is notable that no alpha-like form has been observed. Beta-a is characterized by the short spacings, 4.6, 3.9, and 3.7 and beta-b by spacings, 4.6, and 3.75. Long spacings and m.p.'s appear in Table V.

TABLE V

Long Spacings and Melting Points of 1,3-Diglycerides (30)

Carbons in Fatty Acid Chain	Melting Points °C.	Long Spacings (Å)	
		Beta-a	Beta-b
12	56.8	35.4	37.5
14	66.5	40.6	42.4
16	72.9	44.7	47.4
18	78.2	50.2	52.8

For a given glyceride beta-a is invariably associated with the shorter long spacing. Thus discontinuities in the even homologous series reported by Malkin *et al.* (31) were not confirmed. Beta-a is invariably the first form obtained from the melt but proceeds to beta-b, the only thermodynamically stable form, near the m.p. (at much faster rates for lower than higher homologues). Both forms are obtainable from solvent, high purity favoring beta-b, but the conditions determining the form obtained are not fully established. There is no evidence of characteristically different melting level despite the recognized difference in stability. Short spacing similarities suggest a structural relationship between beta-a and double-chain-length triglyceride structure and between beta-b and triple-chain-length structure. It is not known whether the double-chain-length diglyceride structure involves a fully extended molecule or one in which the two fatty acid radicals are side by side.

Limited evidence on mixed saturated (32) and unsaturated (33) diglycerides suggests highly individualistic behavior for such compounds.

1-Monoglycerides

The crystallization of 1-monoglycerides (34) shows considerable similarity to that of triglycerides. On cooling a melt, an alpha-like form first crystallizes; near its m.p. it goes slowly to beta, the only thermodynamically stable form, obtainable also directly from solvent. An interesting feature is the reversible solid-

solid transformation of metastable alpha to metastable sub-alpha, a lower temperature form. Beta prime, difficult to distinguish from sub-alpha by diffraction pattern, appears to be obtainable only from solvent. It melts above alpha and transforms only to beta, whereas sub-alpha may go either to alpha or to beta. Characteristic short spacing data appear in Table VI.

TABLE VI

Characteristic Short Spacings (Å) for 1-Monopalmitin and 1-Monostearin (34)

Sub-alpha	Alpha	Beta Prime	Beta
4.14 VS	4.64 W*	4.15 VS	4.55 S+
3.92 M	4.18 VS	3.87 VW	4.37S+
3.75 M	3.99 VW*	3.65 W+	3.86 S+
3.56 M	3.81 W*	3.30 W—	3.74 W

* The weak lines are unique for alpha-type patterns.

Long spacings and thermal points for the series 1-monocaproin through 1-monostearin are reproduced in Table VII.

The nearly identical (double-chain-length) long spacing values for the four forms are unusual. In particular, the short value for alpha relative to the presumed molecular length is quite surprising. It suggests a tilted alpha and is at variance with the report of Malkin *et al.* (35).

The sub-alpha to alpha change can be readily followed by dilatometry (34). It was found that the stable beta form is intermediate in density between alpha and the more dense sub-alpha form.

2-Monoglycerides

The 2-monoglycerides are not encountered in ordinary interesterifications and are obtained only by somewhat elaborate synthetic procedures. It has been reported by Daubert *et al.* (36) that series C_{10} through C_{18} shows but one melting point and no other manifestations of thermal breaks, hence is probably free of polymorphism. Solvent crystallized material has been studied by x-ray diffraction (37). The original paper should be consulted for characteristic short spacing values, but the following lines seem to be common to the various individuals of the series, 4.65 S, 4.4 VS, 3.9 VS. Possibly these 2-monoglyceride forms could be regarded as beta, somewhat analogous to the beta of 1-monoglycerides. Long spacings and melting points appear in Table VIII.

The m.p.'s are 10 degrees (more or less) lower than those of the corresponding unsymmetrical monoglycerides and the angles of tilt (i.e. the long spacings) are much smaller.

Application of Polymorphism

The characterization of naturally occurring compounds is commonly difficult and frequently requires application of all the tools at hand in comparing an unknown with standards. Naturally occurring glycerides are not exceptional in this respect.

TABLE VIII

Long Spacing and Melting Points of 2-Monoglycerides (37)

Carbons in Fatty Acid Chain	M.P.°C.	Long Spacing (Å)
10	40.4	29.4
12	51.0	32.8
14	61.2	36.2
16	68.5	40.1
18	74.5	43.8

Polymorphic behavior as a definite step beyond chemical analysis and melting point has been used increasingly to characterize glyceride fractions of natural fats. Thermal points in particular have been used, and a group of such values for a given material is much more conclusive in identification than a single m.p. Diffraction data obviously make identification still more definite.

Polymorphic study has aided in indicating the occurrence of the following triglycerides in natural fats or hydrogenated natural fats — SOS (38, 39), POP (40, 41), OPP, (42), PSS (42), PSP, (41, 42), SPP (42), and SPS (43).

The extraction of 1-monopalmitin from hog pancreas and its identification by m.p. and chemical tests have been reported (44). The nature of the material was further confirmed (45) by polymorphic tests including x-ray diffraction.

The future will certainly see increased application of phase studies to the identification of natural glycerides. This work will proceed more rapidly after careful study has been made of judiciously selected binary (and more complicated) systems of known compounds.

Summary

In order to give a unified picture of recent findings on glyceride polymorphism a review is presented which covers in some detail the saturated single fatty acid triglycerides, the mixed C_{16}-C_{18} saturated triglycerides, saturated diglycerides, and saturated monoglycerides. Mention is made, merely by way of comparison, of unsaturated and saturated-unsaturated triglycerides and unsaturated diglycerides.

The value of a knowledge of glyceride polymorphism in the identification of naturally occurring glycerides is indicated by a number of examples.

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TABLE VII

Long Spacings and Thermal Points of 1-Monoglycerides (34)

Carbons in Fatty Acid Chain	Thermal Points M.P. °C.				Long Spacings (Å)			
	Transition to Alpha	Alpha	Beta Prime	Beta	Subalpha	Alpha	Beta Prime	Beta
10[a]..	8	27	49	53	......	......	......	32.9
12[a]..	15	44	59.5	63	......	......	......	37.3
14[a]..	24	56	67.5	70.5	......	......	......	41.5
16..	39	66.5	74.6	77.0	45.5	45.6	45.25	45.6
18[b]..	49	74	78	81.5	50.3	50.2	50.1	50.1

[a] Data of Malkin *et al.* (35).

[b] An additional reversible thermal change at 42, reported by Malkin *et al.* (35) for 1-monostearin has been confirmed by the present author since the previous publication (34) on monoglycerides, but without explanation by diffraction measurements.

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Compatibility of Derivatives of 9,10-Dihydroxystearic Acid and 9,10-Dihydroxyoctadecanol With Some Commercial Polymers[1]

H. B. KNIGHT, R. E. KOOS, E. F. JORDAN JR. and DANIEL SWERN, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

DURING the course of our program on the epoxidation and hydroxylation of unsaturated compounds derivable from fats (2, 4, 5, 7) we had occasion also to prepare a large number of esters, ether-esters, and hydroxy-ethers of 9,10-dihydroxystearic acid and 9,10-dihydroxyoctadecanol (3, 6, 8, 9). Since these compounds had low vapor pressures, were insoluble in water, and had a relatively high oxygen content, their possible utilization as plasticizers was considered. This paper briefly describes the results of compatibility tests conducted intermittently during the past five years on many of these compounds with some commercial resins. In one case semiquantitative data are also reported.

The compounds studied were the alkyl (8) and alkenyl (9) esters of low-melting 9,10-dihydroxystearic acid, several 9,10(10,9)-alkoxyhydroxyoctadecanols (6), several esters of 9,10(10,9)-alkoxyhydroxystearic acids (6), and two series of previously unreported compounds, namely, esters of the isomeric 9,10-dihydroxystearic acids with ether-alcohols and polymeric plasticizers prepared by the reaction of selected members of this group of new esters with phthalic anhydride. Commercial polymers employed were ethyl cellulose, cellulose acetate, polyvinyl chloride-acetate copolymers (95:5 and 87:13), polyvinyl butyral (low and high viscosity), and in a few cases, polyvinyl acetate, polystyrene, and a vinylidene chloride-acrylonitrile copolymer.

Experimental

Materials Tested. The preparation of the alkyl (8) and alkenyl (9) esters of low-melting 9,10-dihydroxystearic acid, the 9,10(10,9)-alkoxyhydroxyoctadecanols (6), and the esters of the 9,10(10,9)-alkoxyhydroxystearic acids (6) has already been reported.

A typical preparation of an ester of 9,10-dihydroxystearic acid with an ether-alcohol is described. A mixture of 15.8 g. (0.05 mole) of 9,10-dihydroxystearic acid, m.p. 95°, 7.6 g. of ethylene glycol monomethyl ether (0.10 mole), 0.79 g. of naphthalene-2-sulfonic acid, and 200 ml. of toluene was refluxed for eight hours. The water formed during the reaction was removed azeotropically with the toluene, and the toluene was automatically returned to the reaction mixture. The reaction mixture was evaporated to dryness and the residue was washed three times with hot water. The washed, dried residue, consisting essentially of 2-methoxyethyl 9,10-dihydroxystearate, was obtained in quantitative yield and melted at about 45°. Recrystallization from acetone yielded substantially pure product, m.p. 52.3-53.0°, and saponification number, 153 (calcd. 150). Table I lists the esters prepared by the method just described as well as some of their characteristics. All the recrystallized products were white solids whereas some of the crude reaction products were liquids.

Ethylene glycol monomethyl ether, b.p. 123-4°, ethylene glycol monoethyl ether, b.p. 134°, ethylene glycol monobutyl ether, b.p. 170°, ethylene glycol mono(2-ethylbutyl) ether, b.p. 197°, ethylene glycol monophenyl ether, b.p. 170° at 100 mm., ethylene glycol monobenzyl ether, b.p. 180° at 98.5 mm., and diethylene glycol monobutyl ether, b.p. 138° at 50 mm., were obtained by multiple fractional distillation of the purest commercial grades through efficient columns (helix packed or heligrid). Diethylene glycol monomethyl ether, b.p. 192° and diethylene glycol monoethyl ether, b.p. 200-1°, were obtained from the purest commercial grades by washing a benzene solution of the ether-alcohol (250 g. per 750 ml. of solvent) with small quantities of water (ca. 5 ml.) to remove water-soluble materials (10 washes), and fractionally distilling the dried benzene solution.

The polymeric plasticizers were prepared by the reaction of equimolar quantities of methyl 9,10-dihydroxystearate, m.p. 70°, 2-butyoxyethyl-9,10-dihydroxystearate, m.p. 50°, 2-benzyloxyethyl-9,10-dihydroxystearate, m.p. 45°, and 2-(2′-methoxyethoxy)-ethyl-9,10-dihydroxystearate, m.p. 41°, respectively, with phthalic anhydride for one hour at 215-220° and then at 235-240° until the reaction product showed signs of threading. The polymeric plasticizers were pale-yellow to amber colored liquids, insoluble in water.

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.