Phase Behavior of Homologous Series of Monoesters of Polyols

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Abstract

Phase behavior of anhydrous monopalmitates and stearates and of most laurates, myristates and behenates of ethylene glycol, erythritol, xylitol, sorbitol, and mannitol has been studied. The compounds, substantially free of diesters, are mostly not isomerically pure but are predominantly primary esters. Also studied were the (nonisomeric) palmitate and stearate of pentaerythritol (Pe) and the oleate of erythritol. Mesomorphism, absent in anhydrous monoglycerides unless of short chain length and symmetrical, is a prominent feature of the members of the present group of compounds containing at least three unesterified hydroxyls. In general, crystal melting points rise with length of polyol, and mesomorphic melting points rise faster. Crystal melting points rise with acyl chain length while mesomorphic melting points run through a maximum. Heats of fusion are of the order 40 cal/g for crystal melting and 0.5 cal/g for melting of mesomorphic states. In the range explored, mesomorphic values fall with both polyol length and acyl length. At higher acyl chain length, notably with behenates, there are new features of mesomorphic behavior. Crystalline phase, from solvent, melts to a neat or lamellar phase, which in turn melts to liquid with subsequent appearance of higher melting middle or cylindrical phase. Polymorphism is general among the crystal states and tends to be complex. In a brief study of solvent crystallized 50–50 binary mixes of xylitol stearate with other xylitol esters and other stearates, considerable evidence of solid solution in Form I crystals (of xylitol stearate type) was observed with very modest eutectic lowering of crystal melting point. Mesomorphic points were almost linearly intermediate between those of components. Of particular interest were mixtures of xylitol stearate and 1-monostearin (50–50 and 25–75), for which mesomorphic melting points were realized, and for which an extrapolation to 100% monostearin leads to a hypothetical mesomorphic melting point far below any monoglyceride crystalline melting point. A brief examination of an aqueous xylitol palmitate system explored to a maximum temperature of 165 C shows extensive occurrence of aqueous mesomorphic state somewhat after the manner of monoglyceride systems. Mesomorphic melting level rises rapidly from the value for anhydrous ester.

Introduction

Monoglycerides of fatty acids are moderately polar compounds and are effective emulsifiers for oil-water systems. In aqueous systems they form mesomorphic states (1). Anhydrous monoglycerides of higher chain length form no mesomorphic states. Larsson has reported that lower homologs do form such states (2). Monoesters of related polyols are also compounds of interest as emulsifiers. Accordingly a systematic comparative study of a group of monoesters of polyols, chiefly of the type 1,2. . . *n*-hydroxy alkane was carried out. The phase behavior of the anhydrous compounds is here described.

The linear polyols increase in complexity of isomerism as chain length increases. The following were explored: the diol ethylene glycol (not isomeric); one of two tetritols, *m*-erythritol; one of four pentitols, xylitol; and two of eight hexitols, sorbitol and mannitol.

The esters studied were laurate through behenate (except arachidate) of xylitol, sorbitol and mannitol; myristate, palmitate and stearate of ethylene glycol; palmitate, stearate and oleate of *m*-erythritol; and, in addition, the palmitate and stearate of pentaerythritol. Thus palmitates and stearates of each polyol were studied.

The isomerism of the monoesters increases with length of polyol but not in a simple fashion. There is no isomerism with ethylene glycol (or pentaerythritol); there are three isomers of monoglyceride (*d*- and *l*- 1-monoglyceride and 2-monoglyceride); four with *m*-erythritol; five with xylitol; six with sorbitol, but only three with mannitol.

While substantially pure monoesters were prepared, individual isomers were not separated, for the task looms as more difficult by an order of magnitude than the preparation of pure 1- and 2-monoglycerides. Evidence suggests that 1-monoesters did predominate in varying degrees.

Of particular interest among these compounds was the appearance of mesomorphic states at higher tem-

TABLE I
Chemical Analyses of Polyol Monoesters

Polyol[a] ester	Sapon. No.		Hydroxyl No.		Total fatty acid		Periodic acid anal.
	Exp.	Theory	Exp.	Theory	Exp.	Theory	per cent of primary ester value
EgM	203	205.9	203	205.9	84.2	84.2	......
EgP	186	186.7	188	186.7	85.6	85.3	......
EgS	169	171	170	171	86.6	86.6	......
ErP	156	155.6	477	466.9	71.1	71.1	96.5[b]
ErS	143	144.4	446	433.2	73.5	73.2	88.8
ErO	146	145.1	442	435.4	72.1	73.1	96.7
XL	164	167.8	665	671	59.3	59.9	92.3[b]
XM	152	154.8	590	619	62.9	63.0	91.3
XP	141	143.5	573	575	65.4	65.7	95.3
XS	134	134.0	536	536	67.5	68.0	94.8
XB	115	118.2	469	472	71.9	71.8	96.1
SoL	149	153.9	759	770	54.8	55.0	88.0[b]
SoM	138	142.9	697	716	59.1	58.2	88.8
SoP	128.5	133.3	661	667	61.2	59.7	93.4
SoS	121	125.1	616	626	63.5	62.2	93.7
SoB	110	111.1	538	556	66.2	67.5	91.3
MaL	150	153.9	741	770	53.2	55.0	85.4[b]
MaM	144	142.9	687	714	59.1	58.2	86.2
MaP	133	133.3	653	667	61.1	59.7	90.7
MaS	128	125.1	615	626	63.8	62.2	90.2
MaB	105	111.1	548	556	65.2	67.5	......[c]
PeP	148	149.8	443	449	66.8	68.5	......
PeS	135	139.4	416	418	70.0	70.7	......

[a] Abbreviations: Eg, ethylene glycol; M, myristate; P, palmitate; S, stearate; Er, erythritol; O, oleate, X, xylitol; L, laurate; B, behenate; So, sorbitol; Ma, mannitol; Pe, pentaerythritol.
[b] Theoretical value for secondary ester: erythritol 50.5%, xylitol 66.7%, sorbitol and mannitol 75.0% of primary ester value.
[c] Insoluble.

TABLE II

Thermal Data—Melting Points (or Transition Points) C: No Mesomorphic States (by Capillary Melting Point)

Compound	Form 1	Form 2	Form 3	Form 4	Compound	Form 1	(Form 2)
MeS[a] (9)	40.0	....	....	....	EgM	43.8	....
1-Mono S[a] (10)	81.5 (β)	78 (β′)	74 (α)	49[b] (sub α)	EgP	53.5	Fleeting
2-Mono S[a] (10)	74.4	....	....	....	EgS	59.4	Fleeting

[a] Methyl stearate and monoglycerides for comparison.

[b] Transition point (by Thermal Curve).

peratures for all esters of polyols having more than three carbons.

Experimental Procedures

The syntheses of these monoesters were accomplished by interesterification of the polyols at 3:1 and preferably 5:1 molar ratio with methyl ester in dimethyl formamide (DMF) or dimethyl acetamide (DMAc) with approximately 15 ml of solvent per gram of methyl ester. The polyols were ostensibly pure commercial chemicals, not further purified. The methyl ester was better than 98% purity, according to gas liquid chromatography. Benzyl trimethylammonium methoxide (40% in methanol) was employed as a catalyst (about 1 ml/6 g of methyl ester). Alternatively 1% sodium methylate (on a reactant basis) in xylene suspension was used. Reaction with stirring at 100 C and 100 to 120 mm Hg for 3 to 4 hr resulted in distillation of about ¼ of the DMF. The catalyst was inactivated by 15 ml of 50% aqueous acetic acid. (The latter step may be omitted as the catalyst is killed in the subsequent operation.) The hot reaction mix was poured into 2 liters of H_2O. The crude product, maintained in solution by additional solvent if necessary, was further washed three times with H_2O. Because of different polarities and solubilities the compounds had to be worked up differently. While good crude yields were obtained, little effort was made toward obtaining large yields of the purified products. The monoester products were obtained largely by recrystallization. However, crystallization of impurities from the monoester, solvent partition, Soxhlet extraction with acetone (to remove diesters from mannitol monoesters), or column chromatography (in the case of erythritol monostearate) were employed as appropriate. Large excess of polyol in the interesterification step greatly facilitates final purification.

Final purification and recovery was by crystallization. A convenient solvent was benzene-ethanol (5:1). For high melting mannitol esters, DMF was used. Analyses appear in Table I.

The samples were examined by several techniques. For those melting from crystal to isotropic states familiar capillary melting methods were used. Those showing mesomorphic states were examined by differential thermal analysis (DTA) with small (10 mg) samples heated at 10 C/min in the DuPont differential thermal analyzer 900 or the Perkin-Elmer differential scanning calorimeter. The instruments were calibrated over the range of interest with stearic acid (mp 70 C), benzoic acid (123.8 C) and 2,4-dinitroaniline (180.6 C). Routinely, thermal curves were run on solvent-crystallized samples and samples cooled from the isotropic region. Other variations of procedure were used for specific cases. Thermal data are recorded in Tables II and III and Figure 1.

Calorimetric data for the heats of fusion, crystal to mesomorph and mesomorph to isotropic melt were obtained for all saturated esters of linear polyols on the DuPont 900 with calorimeter cell. For calibration, tin (ΔH = 14.2 cal/g at 232 C) (4), indium (ΔH =

TABLE III

Thermal Data—Melting Points (or Transition Points) C: With Mesomorphic States (by DTA ± 1 or 2 C)

Polyol ester[a]	Crystalline states (melting to mesomorphic)		Mesomorphic state (melting to isotropic)
	Higher[b]	Lower[c]	DTA
ErP	83	71	103
ErS	86	78	105
ErO	52	33	71
XL	72	[d]	142
XM	80	47[d,e]	146
XP	85	60[e]	142
XS	92	71[e]	143
XB	96	85[e]	136 (134)[f]
SoL	98		172
SoM	101		184
SoP	107		185
SoS	108	78[e]	185
SoB	108	90[e]	167 (153)[f]
MaL	122 (127–129) (11)		182
MaM	125 (115–122) (11)		185
MaP	124 (128–130) (11)		188
MaS	127 (131–134) (11)		185
MaB	127		174 (161)[f]
PeP	71	62	97
PeS	74	69	98

[a] See abbreviations in Table I.

[b] Form 1 for erythritol, xylitol and sorbitol esters but Form 2 for mannitol and pentaerythritol esters.

[c] Melted and chilled sample hence normally Form 2, but Form 3 for pentaerythritol esters.

[d] May show glassy state.

[e] May show endothermal effect.

[f] Lamellar phase (melts below hexagonal phase).

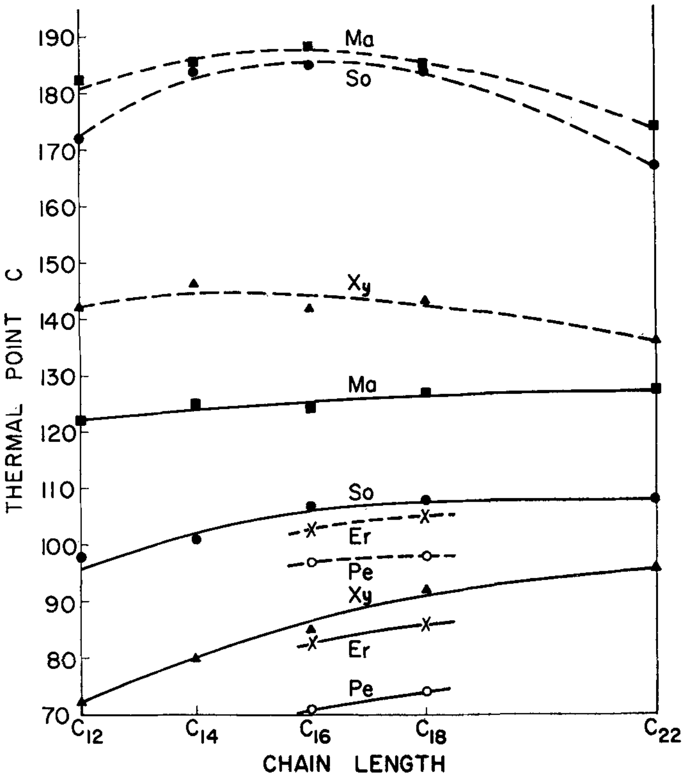

FIG. 1. Thermal points for monoesters of polyols:-X-erythritol, ▲-xylitol, ●-sorbitol, ■-mannitol, ○-pentaerythritol; ———, maximum melting point of crystal to mesomorphic; – – – –, melting point of mesomorphic to isotropic. (See abbreviations in Table I.)

TABLE IV
Long Spacings (A): No Mesomorphic States

Compound			Compound	Form 1	Form 2
MeS[a] (12)	1 Form	47.8	EgM	37.8	.....
1-Mono-S[a] (10)	all 4 Forms	50.2 ± 0.1	EgP	41.6	45.4
2-Mono-S[a] (10)		43.8	EgS	46.0	50.4

[a] For comparison.

6.79 at 147 C) (4) and palmitic acid ($\Delta H = 50.59$ at 62 C) (5) and stearic acid (ΔH by interpolation $= 53.08$ at 70 C) (5) were employed.

X-ray diffraction patterns were obtained on all crystal states to the extent that their stability permitted, on mesomorphic states at lower and higher temperatures and on isotropic states except those of sorbitol and mannitol esters for which it was recognized that decomposition was too rapid to permit a valid result. Patterns were obtained usually at 10 cm sample to film distance on a General Electric film unit with samples in 1 mm O.D. pyrex glass capillaries. Diffraction data appear in Tables IV, V and VI.

The compounds were observed by microscopy on a thermocouple-monitored and roughly calibrated heating stage to confirm levels of change of state, although DTA was much more precise. The mesomorphic states were explored for characteristic microscopic textures.

Melting of mesomorphic states was observed by nuclear magnetic resonance with agreement usually of ±3 C in DTA melting level versus the point of increased proton mobility.

Results and Discussion

The analyses in Table I indicate a purity of the order 95% or better with respect to monoester content.

Another consideration is the primary ester content among the monoesters. Brandner and Birkmeier (3) in an exploration of primary and secondary esters of glycerol and propylene glycol expressed the predominance of primary esters in terms of an equilibrium constant for which they found a value between 3.0 and 4.5. Presumably the same factors are operating in the present case, but the difficulties of purification and analysis militated against exploring quantitatively the proportion of primary and secondary esters. The analyses by periodic acid in Table I do indicate a more than statistical proportion of primary esters and, in the cases of erythritol and xylitol, a great preponderance.

Nomenclature

An object in establishing a system of nomenclature is to interrelate as much information as possible without hiding significant distinctions. In the present case there are two areas requiring decision as to nomenclature, the mesomorphic states and the crystalline states.

Two mesomorphic states are recognized, the neat-like or lamellar state and the middle-like or cylindrical state. These are distinguished by their textures, after the manner of Rosevear (6), since distinction by diffraction pattern, often possible, could not be made because of a paucity of diffraction lines.

The other area is that of the crystalline states. In this case a system of nomenclature applies to each group of compounds, e.g., to the xylitol esters. Form 1 is the form most commonly obtained by solvent crystallization. It is usually the most stable form but not always. In the case of pentaerythritol it is actually a hydrate. Form 1 for a given group of compounds will show, with minor variations, a given set of short spacings, but there is no relationship between one polyol group and another. The long spacings of Form 1 when plotted against chain length are linear. The same considerations hold for Form 2 and for Form 3 with regard to short and long spacings. (The form designated as Form 2 appears to be the stable form for mannitol esters. In the pentaerythritol case, Form

TABLE V
Long Spacings (A): With Mesomorphic States

Compound[a]	Crystalline states				Mesomorphic state		Isotropic state (Bragg spacing)
	Form 1[b]	Form 2[c]	Form 3	Form 4	Low temp. (C)	High temp. (C)	(within 10 C of mesomorphic mp, not over 150 C)
ErP	50.4	49.7	34.6	44.8	34.3 (86)	32.8 (100)	31.5
ErS	54.0	54	36.1	49.2	38 (80)	33.5 (100)	33.0
ErO	49.4				34.2 (55)	34.2 (68)	32.5
XL	27			39.5[d] (IV a)	33 (80)	29 (140)	29
XM	30.3			43.5[e] (IV b)	35 (90)	31.5 (140)	31
XP	32.7	49.0	47.0		41.0 (75)	34 (135)	31
XS	35.5	52.7	51.5		39.0 (100)	35.5 (135)	34
XB	40.5		60	59.8 (IV c)	42.5 (110)	39.5 (130)	37
SoL	41.5				34.5 (110)	34 (150)	
SoM	45.0	48.0			36.8 (115)	34.1 (150)	
SoP	48.0	51.5			39.0 (100)	34.2 (170)	
SoS	51.5	56			40.8 (115)	37.6 (175)	
SoB	58.5	64.3			43 (110)	41.5 (150)	
MaL	39.1	46.5	39.5		32.8 (135)	32.1 (160)	
MaM	42.9	52	44.0	40.3	35 (135)	32 (170)	
MaP	(46.0)	55	47.3	44	38.6 (120)	34.2 (160)	
MaS	49.1	60	51.0	46.2	38.5 (130)	35.3 (175)	
MaB		68.4		64.3 (IV d)	43.5 (135)	42 (160)[f]	
PeP	(31.6)[g]	29.0	30.0		36.2 (80)	34.2 (100)	33.5
PeS	(33.8)[g]	32.1	33		37.5 (80)	35.0 (100)	36.5

[a] See abbreviations in Table I.
[b] Highest melting crystalline state for erythritol, xylitol and sorbitol esters.
[c] Highest melting crystalline state for mannitol and anhydrous pentaerythritol esters.
[d] Unusual short spacings 4.45S, 4.12S.
[e] Form 3 long spacings but Form 2 short spacings.
[f] Six spots suggesting middle.
[g] Probably a hydrate.

TABLE VI
Characterizing Short Spacings[a]

Compound[b]	Form 1	Form 2	Form 3	Form 4
EgM, P, S	4.11S[c]+, 3.91M, 3.70M–, 3.53M	4.12VS, 3.69S—		
Er P, S	4.25S, 4.00M	4.34W, 4.16S, 3.80W[d]	4.6M, 4.0M	4.36S, 4.03W, 3.87W, 3.70W[e]
Er oleate	4.42S, 4.16W, 4.01M, 3.82W	4.26S, 4.02M[f]		
X esters	4.52S+, 3.92S, 3.42M	4.4M+, 4.2S, 3.9W[h]	4.16S, 3.77W+, 3.61W[e]	4.40S, 4.14M, 3.79W+[g]
So esters	4.66S, 4.31W, 4.01W, 3.8W+, 3.6W–	4.75M, 4.60M, 4.21S, 3.65M, 3.30M		
Ma esters	4.57M—, 4.34M+, 4.10M+, 3.63S	4.58S, 3.85M, 3.43M—	5.08M, 4.57S, 4.35S–, 4.14S, 3.57S	4.86S, 4.09S
Pe esters	4.49S, 4.19W+, 3.82S[i]		4.15VS, 3.69M	

[a] Minor variations appear especially between more distant homologs.
[b] See abbreviations in Table I.
[c] VS, very strong; S, strong; M, medium; W, weak; VW, very weak.
[d] Palmitate data.
[e] Stearate data.
[f] Myristate hard to characterize.
[g] Behenate only.
[h] For behenate 4.35S, 3.8W (diff.).
[i] Probably a hydrate.

2 is the solvent crystallized form of anhydrous material.) Form 4, of which there are few examples, is defined less nicely and may exhibit major distinctions among individual esters of a group, but designations "a" or "b" or "c" are used in such cases.

From Figure 1 several facts about the phase behavior of the present compounds are clear at a glance. There is the obvious and expected increase in crystal melting point with increase in molecular weight and chain length of polyol or fatty acid. It is true that other considerations operate, for mannitol esters melt above sorbitol esters, and, at their high melting levels, mannitol esters show little difference in melting point. Erythritol esters melt higher than pentaerythritol esters. For mesomorphic melting points it is clear that polyol length (number of free hydroxyls) is very much of a controlling factor. Also it is clear that meosmorphic melting point passes through a low maximum with increasing acyl length. This is no surprise in principle, since at infinite length the level must fall to the limiting melting point for polyethylene, about 145 C.

Mesomorphic States

The mesomorphic states present a more novel if less complicated picture than that of the crystal states.

A typical well-recognized basis for mesomorphism is the existence in the same molecule of a polar portion and an extended nonpolar moiety as in the classical case of sodium palmitate. In the present case a nonionic polyhydroxyl moiety contributes the polar portion to the molecule. In the present set of compounds it is necessary and sufficient that three free hydroxyls exist in the molecule for meosmorphism to occur. Thus mesomorphic states, absent in anhydrous monopalmitin, have a 20 C range of existence for erythritol palmitate and as much as 75 C for sorbitol palmitate.

While the lengths of a saturated acyl chain, in the range 12 to 22, appear to have a relatively minor influence on the mesomorphic behavior, a significant effect for degree of saturation is seen in the lowering of mesomorphic melting point from 105 C for erythritol stearate to 71 C for erythritol oleate.

Microscopic examination establishes the mesomorphic state, obtained on heating crystals from solvent, as neat-like or lamellar. A short spacing halo, obtained by X-ray diffraction and corresponding to about 4.6 Å is like that of the liquid state, as expected. Long spacing lines show occasionally two or three orders with structural orientation indicated at low temperatures. The long spacing magnitudes, nearly always substantially less than those of the corresponding crystals, decrease at a rate of about 1 A/10 C in keeping with the results of Luzatti et al. (7) who report a coefficient of long spacing expansion of -1 to -2×10^{-3}.

The long spacings of isotropic states, whatever may be their true physical meaning, surely indicate structural features of the order of magnitude of those spacings. They are almost identical to long spacing values of corresponding mesomorphic states at high temperatures; they probably indicate micelles, perhaps reversed spherical micelles with polar cores and hydrocarbon exteriors.

One of the striking features of the present study was the appearance, particularly in behenates, of a cylindrical or middle-type mesomorphic state melting above the corresponding lamellar state. The effect was evident both by DTA and microscopy and more strikingly with mannitol and sorbitol than with xylitol ester. As, e.g., mannitol behenate was warmed slowly near the lower mesomorphic melting point (about 161 C), melting of lamellar phase was seen to occur under the microscope followed by "nucleation" of cylindrical or middle-type phase. At constant temperature, the entire specimen "crystallized" in the

TABLE VII
Binary Mixes (50–50)

Other monoester[a]	Long Spacings A		Thermal Points C		
			Crystal mp		Mesomorphic mp
	Exp. (from solvent)	Components	From solvent	Melt, chill	
Xylitol monoester mixes with xylitol monostearate					
XL	31.5[b]	35.5,27 (31.3)[c]	73	[d]	142
XM	32.9[b]	35.5,30.3(32.9)	77	55?	145
XP	34.3[b]	35.5,32.7(34.1)	82	63	144
XB	38.4[b]	35.5,40.5(38.0)	87	75	139
Polyol monostearate mixes with xylitol monostearate					
ErS	35,55[e]	35.5,54.0	81	74	120
SoS	36,49[e]	35.5,48	87(96)	56,72	164
MaS	36,49(weak)[f]	35.5,49	88	56,107	165

[a] See abbreviations in Table I.
[b] All Form 1 in crystalline state.
[c] Average.
[d] Glass.
[e] Definitel XS, Form 1 type, with a second significant phase.
[f] Largely XS, Form 1 type, with possible second phase.

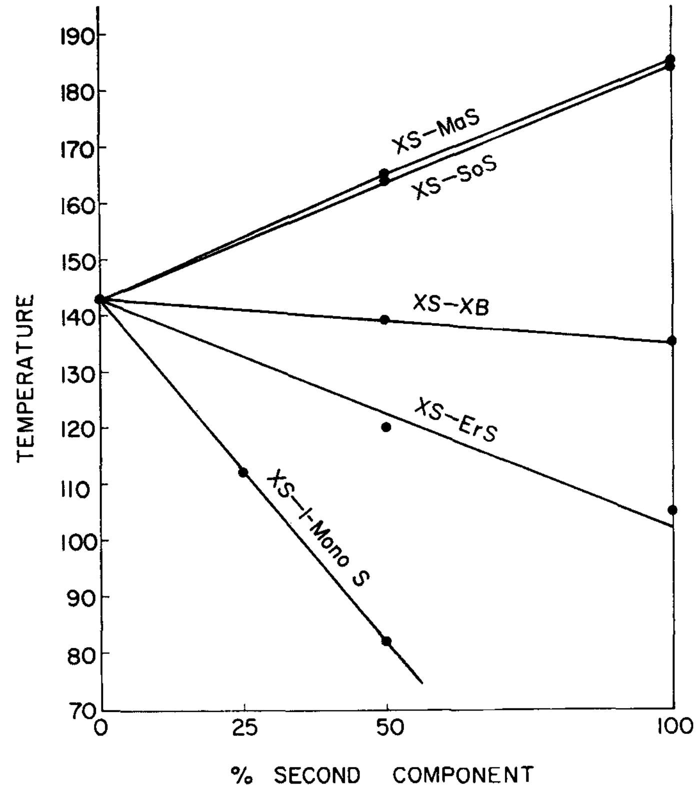

FIG. 2. Mesomorphic phase melting points of xylitol stearate with a second component. (See abbreviations in Table I.)

new mesomorphic phase which then melted several degrees higher (at about 174 C). On subsequent cooling either into the mesomorphic or crystalline region no other mesomorphic phase than cylindrical or middle-type ever appeared in the mesomorphic region. Although unconfirmed by x-ray diffraction, which typically gave but a single long spacing line, there seems no doubt that one sees melting of metastable lamellar and development of more stable middle-type mesomorph, but it is not yet certain that middle-type is stable over the whole mesomorphic range for behenates.

Related behavior was observed with stearate and palmitate esters. On melting lamellar phase to isotropic and cooling, batonnets (small rods) reminiscent of middle would develop and in some instances true middle texture. Typically, however, these batonnets would fade under crossed nicols on further cooling and give way to typical lamellar texture. Repeated heating would stabilize the middle texture, presumably by some obscure influence of partial decomposition.

It seems clear that there occurs some such sequence as this on melting solvent crystallized mannitol behenate; crystals, with prominent regions of polar sheets, melt to lamellar mesomorphic states with polar sheets. These in turn melt to micellar (perhaps spherically micellar) isotropic regions which "nucleate" as collections of strings of spheres or collections of cylinders of the middle-type phase. These cylinders may well have polar interiors. On cooling, the middle phase produces crystals (generally if not always of different polymorphic state from that obtained from solvent) in which the polar sheets are not so dominant or not so extensive, so that their subsequent melting results in a return to middle and not to lamellar phase.

Crystal States

It is difficult to summarize the crystalline states of the several compounds reported here. A high degree of polymorphism, diversity among compounds from different polyols, diversity even among homologous esters from a given polyol due, in part, to differences in isomeric purity combine to complicate the task.

First, it may be instructive to compare esters from the different polyols, e.g., the stearates, as tabulated in Tables II, III, IV and V and including methyl stearate and monostearins, previously reported.

Methyl stearate is monomorphic, exhibiting a tilted form of 0⊥ subcell type.

Ethylene glycol monostearate is dimorphic. Form 1, from solvent is a tilted form of 0⊥ subcells. Form 2, from melt and giving the same thermal point as Form 1, is a form of perpendicular chains and also of 0⊥ subcell type.

The complicated polymorphism of 1-monostearin has been often reviewed, recently by Larsson (8). A difference in behavior exists between the racemic compound and an enantiomorph. Present interest is in racemic monostearin. It shows at least four tilted forms of very nearly equal long spacings. According to Larsson, closely related to the stable form is a fifth state. Metastable forms from melt, one clearly of α-type, are reversibly transformable into each other. The 2-monostearin is monomorphic.

Erythritol stearate was difficult to characterize. Four forms occur, Form 1 from solvent but usually not alone.

Xylitol stearate shows three forms, a highly tilted form from solvent, and two other less tilted forms under other conditions.

Sorbitol esters are among the simpler compounds in behavior. The stearate is dimorphic, with the more tilted Form 1 from solvent.

Mannitol stearate is complex in behavior. Form 1 from solvent is more titlted than the more stable Form 2. Two other highly tilted forms are encountered.

Pentaerythritol stearate exhibits a hydrated form, here called Form 1. The anhydrous ester shows two forms. All three forms are of nearly equal long spacing.

Now, a consideration of individual esters among the various groups of compounds is in order.

The ethylene glycol esters studied behave similarly except that Form 2 for myristate appears to be too fleeting to give a diffraction pattern.

TABLE VIII
Mixes of 1-Monostearin With Xylitol Monostearate

Other monoester	Long Spacings A		Thermal Points C		
			Crystal mp		*Mesomorphic mp*
	Exp. (from solvent)	Components	From solvent	Melt, chill	
50% 1-Mono S	35.5,50[a]	35.5,50.1	76,80	74	82
25% 1-Mono S	36,51[a]	35.5,50.1	76,85	73	112

[a] Definitel XS, Form 1 type, with a second significant phase.

TABLE IX
Heats of Fusion (cal/g)

Polyol	Stable Crystal to Mesomorph					Mesomorph to Isotropic Melt				
	L	M	P	S	Be	L	M	P	S	Be
Erythritol			36.2	39.3				0.53(0.60)[a]	0.36(0.44)	
Xylitol	35.9	35.5	42.9	46.2	47.9	1.29(1.06)	0.79(0.74)	0.64(0.50)	0.34(0.34)	0.25(0.27)
Sorbitol	32.6	32.1	36.0	40.4	40.8	0.86(0.95)	0.49(0.64)	0.48(0.40)	0.26(0.24)	0.21(0.16)
Mannitol	34.1	32.1	34.1	34.7	35.3	0.95(0.95)	0.46(0.64)	0.47(0.40)	0.37(0.24)	0.17(0.16)

[a] Calculated according to Equation 4.

The erythritol esters are somewhat intractable. Form 1 is obtained from solvent, Form 2 generally from melt. Other forms are obtained under diverse conditions not clearly defined and are often in mixture with Form 1.

Xylitol esters from solvent uniformly show a highly tilted Form 1. From melt their behavior is diverse. The laurate and myristate, on quick chilling, form glasses which with heat and time change to crystalline states.

The sorbitol esters are reasonably simple and uniform in behavior. A more highly tilted Form 1 from solvent is replaced, on melting and chilling an ester, by a less tilted Form 2 except for monomorphic laurate.

The mannitol ester behavior is perhaps most complex of all. Form 1 is obtained from solvent for all but behenate, but the stable form obtained on heating is Form 2, obtained from solvent for behenate. Other forms are obtained by other treatments.

Pentaerythritol esters presented serious problems because of the hydration of the palmitate, especially. As normally prepared from solvent, palmitate gave Form 1 whose DTA behavior was anomalous. After drying over P_2O_5 with a loss of 4.5% H_2O (4.7% for monohydrate) Form 2 was obtained with DTA behavior closely correlating with monostearate. Form 3 was obtained from melt. As normally prepared, the stearate was in Form 2, but early (presumably more hydrous preparations) contained Form 1.

It is unusual for long spacings of the mesomorphic state to exceed those of the crystalline state as clearly occurs in the case of pentaerythritol esters and in the case of Form 1 of xylitol esters. The phenomenon is surely correlated with occurrence of a large (but perhaps, not too large) polar group which in certain crystal alignments causes the chain to assume a low angle of tilt. It is worthy of note that even in such cases long spacings of crystals in a homologous series increase at a greater rate than do long spacings of a mesomorphic state (in both cases presumably for double-chain-length structures).

Calorimetric Studies

Approximate values for heats of fusion, ΔH, of the saturated esters of linear polyols appear in Table IX. The values for crystal to mesomorphic melting are in the range of 40 cal/g, and for mesomorphic to isotropic melting in the range of 0.5 cal/g.

Equations obtained graphically for stable crystal (to mesomorph) melting of the various groups of esters are as follows:

$$\Delta H_X = 16.0 + 1.53\ A, \text{ for xylitol esters} \quad [1]$$

$$\Delta H_{So} = 18.0 \pm 1.12\ A, \text{ for sorbitol esters} \quad [2]$$

$$\Delta H_{Ma} = 31.4 + 0.16\ A, \text{ for mannitol estres} \quad [3]$$

where A is the number of carbons in acyl group. It appears significant that the coefficient of A is a sensitive function of melting level of the ester group. The constant may be so, also.

For mesomorph melting the following least squared equation fits the data moderately well as seen in Table IX for all the saturated polyol esters.

$$\Delta H = -0.101\ P - 0.419\ A + 0.0100A^2 + 5.148 \quad [4]$$

where P is the number of carbons in polyol and A is the number of carbons in the acyl chain.

Aqueous Xylitol Palmitate System

An aqueous xylitol palmitate system with mixes of 2.5, 5, 7.5, 10, 15, 20, 30 and 40% H_2O was explored in constricted sealed tubes (centrifuged back and forth at 100 C for mixing) over the range 25–165 C after the manner of previous studies with aqueous monoglyceride systems (1). Mesomorphic melting level (of lamellar phase) rises rapidly from 142 C, the level of anhydrous ester, to about 160 for 2.5% H_2O. Crystal melting point appears to drop with addition of H_2O, but metastability makes observation difficult. No viscous isotropic phase was observed nor any evidence of middle-like state.

Binary Mixes

A brief exploration of several solvent crystallized 50–50 binary mixes involving xylitol stearate as one component showed extensive formation of solid solutions corresponding to Form 1 type of xylitol stearate and with eutectic lowering of crystal melting point and with linearly intermediate mesomorphic melting points. See Table VII and Figure 2. Mixtures of xylitol stearate and 1-monostearin (both 50% and 25% of the 1st component) (Table VIII) show mesomorphic melting points which, when extrapolated to 100% monostearin, indicate a hypothetical value much below any crystalline melting point of 1-monostearin.

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REFERENCES

1. Lutton, E. S., JAOCS *42,* 1068 (1965).
2. Larsson, K., "Proceedings of the Meeting of International Union of Crystallography," International Union of Crystallography, Moscow, 1966.
3. Brandner, J. D., and R. L. Birkmeier, JAOCS *41,* 367 (1964).
4. American Institute of Physics, "American Institute of Physics Handbook," McGraw-Hill Book Co., New York, 1957.
5. Garner, W. E., F. C. Madden and J. E. Rushbrooke, J. Chem. Soc., *1926,* 2491.
6. Rosevear, F. B., JAOCS *31,* 628 (1954).
7. Luzzati, V., H. Mustacchi and A. Skoulios, Nature *180,* 600 (1959).
8. Larsson, K., Arkiv Kemi *23,* 35 (1964).
9. Lutton, E. S., and F. R. Hugenberg, J. Chem. Eng. Data *7,* 208 (1962).
10. Lutton, E. S., JAOCS *27,* 276 (1950).
11. Reinefeld, E., and G. Klauenberg, Tenside *9/10,* 267 (1968).
12. Francis, F., and S. H. Piper, J. Am. Chem. Soc. *61,* 577 (1939).

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