Preparation and Phase Behavior of Positionally Isomeric Propylene Glycol Monoesters

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Abstract

Primary even-chain-length monoesters of propylene glycol (1,2-propanediol), myristate through behenate, have been prepared, and also the secondary monostearate. Phase behavior of the pure compounds and of the binary system of isomeric stearates has been studied. This behavior is one of considerable complexity. The highest-melting stable form of the primary stearate is a single-chain-length (SCL) perpendicular form (Form II) of very weak long-spacing intensities. A metastable perpendicular double-chain-length (DCL) α form occurs at the (metastable) melting point after chilling the primary esters; it transforms to a perpendicular DCL Form III on cooling. Low temp crystallization from dilute hexane gives a tilted DCL Form I, the typical room temp form in crude preparations of primary ester. The secondary stearate exhibits a single similar DCL Form I at 25C and a perpendicular SCL α form just under the melting point of the chilled melt. Polymorphism is modified by mol wt and purity. Primary arachidate and behenate do not show Form II, hence show stable α at their (stable) melting points.

Repeated crystallization of the 80% primary ester obtained on direct esterification with stearic acid yields pure primary ester. Special synthesis via 1-tetrahydropyranyl propylene glycol is necessary to prepare pure secondary ester. The pure primary monobehenate could be obtained only by acylation of 2-tetrahydropyranyl propylene glycol obtained by reduction of tetrahydropyranyl ethyl lactate. Removal of the tetrahydropyranyl blocking groups was accomplished without acyl migration by using boric acid as a cleaving agent.

Introduction

PROPYLENE GLYCOL (1,2-propanediol) mono fatty acid esters are a group of moderately surface-active compounds which have proved to be effective emulsifiers or additives for shortening, in cake-baking for example (1). Combinations with monoglycerides are also effective (1b,2,3). While relatively easy to prepare as isomeric mixtures, they are relatively difficult to obtain as pure (racemic) position isomers. The percentages obtained in preparations of these isomers have been discussed by Brandner et al. (4) but without description of the individual isomers.

The phase behavior of this group of compounds presents many interesting features. The binary system prepared from pure primary and secondary stearates is a notable example of complex polymorphic behavior.

This paper covers the preparation of primary 1,2-propylene glycol monoesters of even fatty acids—myristic through behenic—also the secondary monostearate. Phase behavior of all individual compounds was studied and also that of the binary system of primary and secondary stearates.

Some evidence on the phase behavior of the propylene glycol monopalmitate and monostearate has been reported by Kuhrt et al. (5). Present results agree with most of their evidence.

In referring to the monoester of 1,2-propylene glycol and stearic acid, it is customary to speak of propylene glycol monostearate (1). Therefore, to distinguish the primary and secondary esters, the terms 1-propylene glycol monostearate (1-PGMS) and 2-propylene glycol monostearate (2-PGMS), respectively, are used.

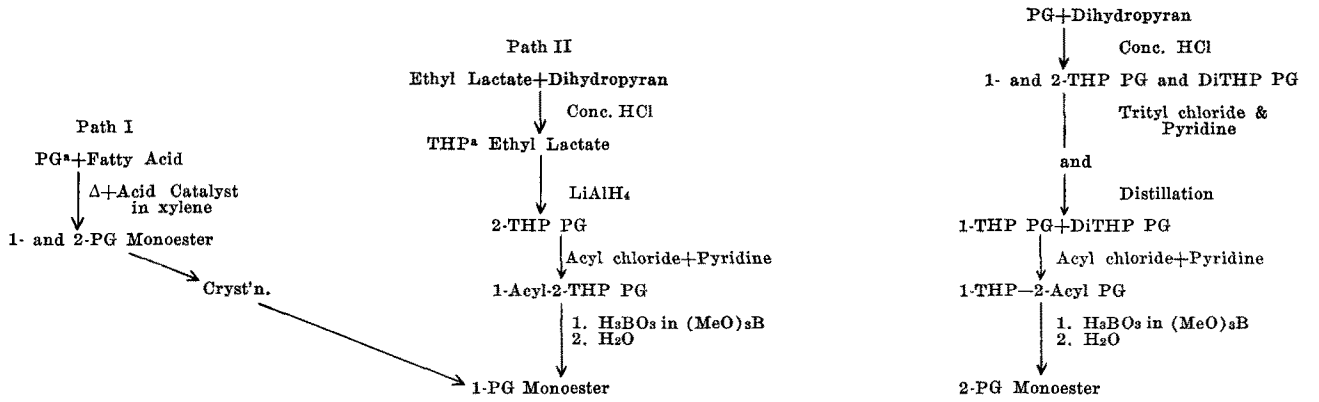
While position isomerism only has been considered in these introductory remarks, it should be noted that asymmetry exists in both the 1- and 2-positional isomers leading to the existence of pairs of *d*- and *l*-isomers. The products of this report are all racemic mixtures.

The pathways to the 1-propylene glycol monostearate (1-PGMS) and 2-propylene glycol monostearate (2-PGMS) of this work are shown diagrammatically in Reaction Scheme (Fig. 1). Synthesis via the blocking agent dihydropyran, as reported for other fatty syntheses (6), was employed. In referring to intermediates, "1-tetrahydropyranyl (THP)," indicates attachment to make an ether linkage at the 1- or primary position of propylene glycol (and the 1-position of the THP group). The tetrahydropyranyl ether then constitutes an acetal which is acid-labile, leading to easy removal by boric acid without migration of an adjacent acyl group.

Preparation of Isomerically Mixed PMGS. The amt of 425 g stearic acid (1.5 moles) was reacted with 1140 g propylene glycol (15 moles) plus 9 g *p*-toluenesulfonic acid in 2.15 liters xylene by heating the materials at reflux under a moisture trap for 3 hr. The hot products were poured onto ice with stirring. The xylene and aqueous layers were separated and the xylene layer was water-washed 3 times. The xylene layer was dried with anhydrous sodium sulfate, filtered, and diluted with 6 liters of hexane. The PGMS was crystallized at −18C. The crystals were redissolved in 4 liters of hexane and crystallized at 5C. The crystallization from 4 liters of hexane at 5C was repeated, yield 300 g PGMS (58%) of an isomerically mixed nature.

Isolation of 1-PGMS. The isomerically mixed PGMS was dissolved in 7 ml of hexane per gram of PGMS. This solution was crystallized at 18C after seeding with high-melting (53C) isomerically mixed PGMS (the high-melting form being produced by aging the low melting form for 3 weeks at 38C or by previous seeded crystallization). The crystallization at 18C required 1 week since the growth of crystals was slow. The crystallization process (preferably each time with seeding) was repeated, once at 18C and once at 21C. A yield of 31.4 g of 1-PGMS was obtained. This product is 1-PGMS of 100% purity based on lipase assay (7) for configuration purity. Analytical characterization of this product is given in Table I. (Methods for determining the isomeric composition of isomerically mixed propylene glycol monoesters and also the equilibrium composition of equilibrated monoesters by lipase assay and IR spectrometry of solutions will constitute a separate report.)

Preparation of 1-Propylene Glycol Monobehenate (1-PGMB). It has not been possible to isolate the isomercially pure 1-propylene glycol monoesters of the C_{20} and C_{22} fatty acids by fractional crystallization. Failure to crystallize in a form analogous to the stable



[a] THP = tetrahydropyranyl; PG = propylene glycol; THP PG = tetrahydropyranyl ether of PG.

FIG. 1. Reaction scheme: Isomeric propylene glycol mono esters by isolation and/or synthesis.

form of 1-PGMS may be a contributing factor. The following direct synthesis has been resorted to for preparation of 1-PGMB.

Tetrahydropyranyl Ethyl Lactate: Ethyl lactate, 450 g (3.8 moles), was mixed with 1.2 ml concd hydrochloric acid and the mixture was cooled in an ice bath. Dihydropyran 420 g (4.9 moles) was added with stirring after which the sample was allowed to warm to room temperature. After 3 hr, 10 g of potassium carbonate was added and the sample was stirred.

The product was distilled under reduced pressure with collection of 366 g tetrahydropyranyl ethyl lactate boiling at 65–70C at 1–2 Torr., yield = 47%. See Table I for properties and analysis.

2-Tetrahydropyranyl Propylene Glycol: Tetrahydropyranyl ethyl lactate, 82 g (0.46 mole), was dissolved in 300 ml tetrahydrofuran. Lithium aluminum hydride, 8.5 g, was added to 500 ml tetrahydrofuran and the slurry was cooled in an acetone-ethanol dry-ice bath. The tetrahydropyranyl ethyl lactate solution was added slowly to the lithium aluminum hydride slurry and subsequently the mixture was warmed to room temp. The reactants were diluted with 150 ml ethanol followed by 2 liters of water. The sample was then extracted three times with 400 ml portions of benzene. The benzene extracts were dried with sodium sulfate, filtered, and the filtrate was distilled with collection of the fraction boiling at 78–81C at 3 Torr. The yield was 28 g (38%). Analyses of the products are given in Table I.

1-Behenoyl-2-Tetrahydropyranyl Propylene Glycol: 2-Tetrahydropyranyl propylene glycol, 16.0 g (0.1 mole), was inter-esterified with 39 g methyl behenate and with 4 ml of 40% trimethyl benzyl ammonium methoxide as catalyst. The reactants were stirred in a 250 ml flask heated at 60–80C under a reduced pressure of 200 mm Torr. for 6 hr. The contents were poured into 600 ml of hexane, and the hexane solution was washed with 400 ml of 1% potassium bicarbonate solution. The washed hexane layer was diluted with 200 ml ethanol and 75 g urea was added to the sample. Adduct formation with urea was accomplished by stirring the sample initially at 40C and allowing the mixture to cool at 25C during a 2-hr interval. The urea adduct was removed by filtration and discarded. The adduction with urea was repeated with 60 g of urea. The filtrate from the second urea adduction was water-washed three times, and the hexane layer was evaporated to dryness. The residue was dissolved in 300 ml of hexane, and the solution was crystallized at −18C. Filtration at −18C yielded 21.3 g, 44% yield. Thin-layer chromatography indicated the absence of impurities of greater than 1% concn in this intermediate.

1-Propylene Glycol Monobehenate (1-PGMB): 1-Behenoyl-2-tetrahydropyranyl propylene glycol, 8 g (0.0165 mole) was cleaved by reaction with 11 ml of 1.6-molar boric acid in trimethyl borate. The reactants were heated in a boiling water bath with application of vacuum. Heating was continued for 15 min with 2–5 mm Torr. during the final 10 min. The residue was cooled to room temp and dissolved in 200 ml ethyl ether and water-washed three times. The ether phase was dried with sodium sulfate, and evaporated to dryness on an evaporator without warming above 30C. The residue was dissolved in 100 ml petroleum ether, bp 30–40C, and crystallized at 21C. The crystals recovered at 21C were recrystallized at 10C from 200 ml petroleum ether, bp 30–40C, yield 4.6 g (67%). Thin-layer chromatography showed the product to be homogeneous with no impurities at a concn of 1% or more. Analytical data and properties are given in Table I.

TABLE I

Properties and Analytical Data for 1- and 2-PGMS and 1-PGMB and Intermediates

Compound[a]	Yield %	CMP °C	BP °C	BP mm. Hg. Press.	Analyses S.V. Calc.	S.V. Obs.	H.V. Calc.	H.V. Obs.	A.V. Obs.	% C Calc.	% C Obs.	% H Calc.	% H Obs.
1-PGMS[b]	10	55.9			164	165	164	169	0.1	73.6	72.7	12.27	11.85
PGMS (mixed isomers)	60	45			164	166	164	161	2.4		—		—
2-PGMS[b]	55	40.6			164	162	164	163	0.6	73.6	73.7	12.27	12.4
1-THP-2-PGMS[b]	78	14			132	130	0	0	0	73.3	72.6	11.74	11.7
1-THP-PG[c]	5	—	60–64	0.3	0	—	351	312	—	59.9	59.8	10.0	9.9
1-PGMB[b]	69	62.1	—		141	138	141	139	0.1	75.4	75.4	12.56	12.6
2-THP-1-PGMB[b]	42	42.3	—		116	115	0	0.7	0	74.4	74.8	11.98	11.9
2-THPPG[d]	40	—	78–81	3	0	2	351	310	—	59.9	60.3	10.0	10.0
THP Ethyl Lactate	47	—	68–71	1	275	256	0	0.6	0	58.8	57.9	8.82	9.0

[a] Components are identified as follows: PG = propylene glycol, MS = monostearate, MB = monobehenate, THP = tetrahydropyranyl ether.
[b] TLC (Thin Layer chromatography) shows these materials to be of high purity (99+%).
[c] TLC indicates approx 5% impurity, this being the di-THP PG.
[d] TLC indicates no more than 5% impurity, but the sample contains two major components; interpreted to be the erythro and threo diastereomers.

TABLE II
Thermal and Diffraction Data for Propylene Glycol Monoesters

	Primary Esters (1-PGM-)					Secondary Esters
	M	P	S	A	B	2-PGMS
THERMAL DATA °C						
Trans. pt. to α	11.5	28.5	38.5	43	51	<38[a]
α mp	23.1	37 [36.5 (5)]	47.1 [46.5 (5)]	53.8	62.1	40.6
Stable form mp	35.5	45 [42.5 (5)]	55.9 [56.5 (5)]	54.5	62.1	40.6
	Long-Spacings Magnitudes in Å					
DIFFRACTION DATA						
Form II	24.6	27.0	29.4	——	——	
α	——	45.8	52.5	57.3	62.3	29.6
Form III	——	48.4	53.4	——	62.3	
Form I	39.7[b]	44.1[b]	48.5	52.3	56.8	47.7
	Characteristic Intensity Values for Different Orders of Long-Spacings					
	(Primary Esters)					(Secondary Esters)
Form II	2W, 6W					——
α	1VS,4M, 6M–, (8VW)					1W
Form III	1VS, 2W, 4M, 5W, 6M–, (8VW)					——
Form I	1VS, 4M+, 6M, 7VW, 8VW					1VS, 3W+, 4M, 6M, 8W
	Characteristic Short-Spacings					
	(Primary Esters)					(Secondary Esters)
Form II	9.75M, 4.07VS, 3.66S					
α	4.13S (4.5, 3.95, 3.85—all W)					4.13S
Form III	4.14VS, 3.79S					
Form I	4.20W, 4.04S, 3.79M, 3.64M, 3.48W					4.32W, 4.20S, 4.06W, 3.67M

[a] On melted and chilled sample.
[b] On impure preparations.
VS—very strong, S—strong, M—medium, W—weak, VW—very weak.

Preparation of 2-PGMS. Mixed Tetrahydropyranyl Ethers of Propylene Glycol: A solution of 3 ml concd hydrochloric acid in 500 g (6.6 moles) propylene glycol was cooled in an ice bath. Dihydropyran, 330 g (3.93 moles) was added at a rate to keep the mixture below 40C. (The reaction is very exothermic.) One hour after the addition was completed, the sample was treated with 20 g potassium carbonate with stirring. The organic layer was filtered and subsequently washed twice with small portions of 5% aqueous potassium carbonate solution. The organic phase was dried over anhydrous K_2CO_3 and distilled from the K_2CO_3 under reduced pressure. A distillate of 403 g, boiling above 70C at 10 Torr. was collected.

1-Tetrahydropyranyl Propylene Glycol: Mixed tetrahydropyranyl ethers of propylene glycol, 200 g (1.25 moles) were mixed with 130 g trityl chloride in 150 ml dry pyridine. The reactants were stirred at room temp 15 min, then held for 18 hr at 50C. The product was cooled and diluted with 1 liter of water, and the water layer was extracted with 1 liter ethyl ether. The ether solution was distilled with collection of a distillate fraction boiling between 50 and 140C at 1–2 mm Torr. The distillate was redistilled through an 18-in. Vigreux column with recovery of a distillate fraction of 26.5 g, bp 60–64C at 0.3–0.4 Torr. The 26.5 g distillate fraction was primarily 1-tetrahydropyranyl ether of propylene glycol slightly contaminated with the ditetrahydropyranyl ether of propylene glycol. See Table I for analytical characterization.

1-Tetrahydropyranyl-2-Stearoyl Propylene Glycol: 1-Tetrahydropyranyl propylene glycol, 8 g (0.05 mole) was dissolved in 100 ml of water-washed, distilled and dried chloroform plus 10 ml pyridine. Stearoyl chloride, 16 g, in 30 ml of purified chloroform was added with stirring. The sample was held at 27C for three days, then diluted with petroleum ether, bp 30–40C, and washed successively with water, cold 1% hydrochloric acid, 1% disodium hydrogen phosphate solution and finally three times with water. The solvent was evaporated without warming above 40C, and the residue was dissolved in 400 ml acetone, after which the solution was stirred with 40 g of urea for three hours at 27C. The urea adduct was filtered out and discarded. The filtrate from the urea adduction was diluted with 500 ml petroleum ether, bp 30–40C, water-washed, and treated with 15 g of Amberlite IRA-400 resin in the hydroxide form to remove residual traces of free fatty acid. The slurry was stirred for 30 min, and filtered. Evaporation of the filtrate yielded 16.5 g of 1-THP-2-stearoyl propylene glycol, 77% yield.

2-Stearoyl Propylene Glycol (2-PGMS): 1-Tetrahydropyranyl-2-stearoyl propylene glycol, 5 g (0.0117 moles), was mixed with 7.5 ml of 1.6-molar boric acid in trimethyl borate. The reactants were warmed slightly and then heated at 85C in a water bath for 10 min under reduced pressure which eventually reached 2–3 mm Torr. The sample was cooled to room temp, and the residue was taken up in 200 ml of ethyl ether. The ether solution (and a slight amt of insoluble resi-

TABLE III
Tabulation of Thermal Data °C on 2-PGMS—1-PGMS System

% 1-PGMS	Temp[a] α Observed	Rapid C.M.P. (α State)	C.M.P. (melt, chill)	C.M.P. (melt, chill, 1 wk, 100°F.)	C.M.P. Solvent-Crystallized, (without fractionation)	Form I Long-Spacings	α Long-Spacings
0	38	40.3	40.3	40.7	40.1	47.7	29.6
20	38	41.1	41.1	41.4	41.4	48	29?
35	40.5	41.2	41.4	41.8	42.1	48	29?
50	40.5	42.5	42.7	42.7	43.0	48	49.0
65	42	43.9	44.2	44.2	44.2	48	50.0
80	42	45.4	45.4	45.4	49.4	48	49.5
100	42	47.1	47.4	54.5	55.9	48.5	52.5

[a] By x-ray diffraction, after melting and chilling.

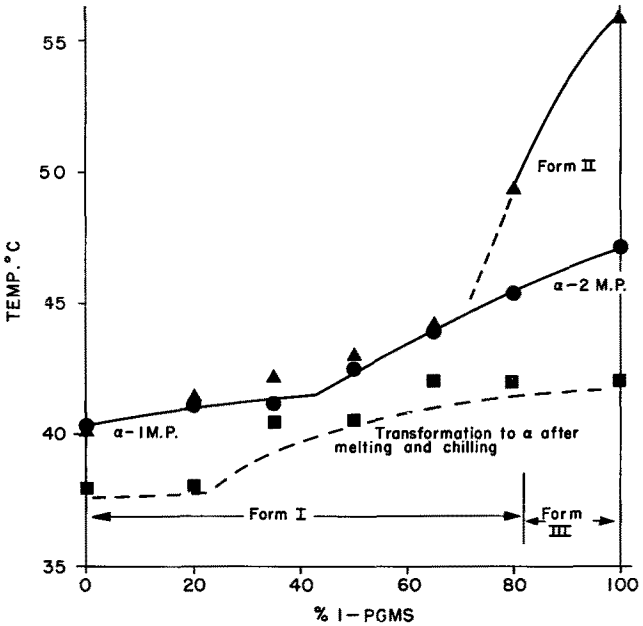


FIG. 2. The Binary System 2-PGMS—1-PGMS. • Rapid C.M.P. (after melt, chill); ■ α observed by x-ray after melt, chill; ▲ C.M.P. after solvent crystallization.

due) was water-washed three times. The ether phase was dried with 20 g sodium sulfate and filtered. The ether was removed by evaporation without warming above 30C. The residue was dissolved in 100 ml petroleum ether, bp 30–40C and 2-PGMS was crystallized at 0C, yield 2.2 g, (55%).

Phase Study. Most of the experimental procedures for phase study have been described in previous publications from this laboratory (8).

Two melting-point procedures were used—"rapid complete melting points" and "regular complete melting points." Such information was supplemented by differential thermal analyses (DTA) on 0.3–0.4 g samples in a triple-welled copper block with one sample well, one mineral oil control well and (usually) a third mineral oil program well. The DTA data were used especially for study of transformations in metastable states, transformations to α being located by determination of their difference from corresponding α melting levels.

Flat-film x-ray diffraction patterns were obtained for all polymorphic forms either as rod pellets or in thin-walled Pyrex glass capillaries with a General Electric XRD-1 unit employing CuKα radiation (nickel-filtered) and a 0.025 pinhole system. Sample-to-film distance was normally 5 cm, but was 10 cm for determination of long spacings.

Thermal and diffraction data are listed in Table II.

For the study of the binary system 2-PGMS—1-PGMS, mixes were prepared from the pure components. Thermal data for the binary system are given in Table III and Figure 2.

Results and Discussion

The Various Polymorphs of 1-PGM-esters.—Form II—obtained with 1-PGMM, P and S (myristate, palmitate and stearate) appeared on crystallization from hexane but also on transformation of metastable forms at room temp, in a matter of a few weeks for PGMS. At first glance the diffraction pattern of Form II resembles those of I or III, but its 9.75Å intermediate spacing and very weak long-spacings are distinctive. The long-spacings by their entirely different character and difference in relative intensity of different orders bespeak a difference from the normal head-to-head DCL structure of other forms; the 9.75 spacing corresponds to double the a or b axis value encountered in unit cells of many long-chain phases. Accordingly, it is postulated that Form II is a SCL structure with the structural unit being a pair of reversed chains. Calculated intensities based on a one-dimensional Fourier analysis of this model were in fairly good agreement with experiment.

The α phase, obtained in a limited range below the rapid complete mp, is actually stable for 1-PGMA (arachidate) and −B but metastable for 1-PGMP and −S. While indicated by thermal data, α was too fleeting in PGMM to give a diffraction pattern. For PGMS, −A and − B, α appears to be of familiar DCL type and slightly tilted, but the small long-spacing value for PGMP suggests increased tilting. No reason is known for this discrepancy among the homologs. There appear to be weak extra α phase lines which for 1-PGMP and -S occur at approx 4.5, 3.95 and 3.8Å. (With respect to the tilted structure and extra short-spacing lines, the α form of 1-PGMS is reminiscent of 1-monostearin.)

Form III, a metastable form for pure-1-PGMP and −S, appears to be the stable form of 1-PGMB at room temp. The short-spacings suggest a cross-sectional pattern slightly modified from the familiar 0⊥ type (9) in that its short-spacings are closer together than normal. It is a slightly tilted DCL structure. It is obtained by chilling the melt (but in the case of 1-PGMB may be mixed with Form I) and it transforms to α about 10C below the melting point.

Form I is also a metastable DCL form, but of more familiar 0⊥ cross-sectional type and more tilted. It has been obtained for 1-PGMS and 1-PGMB by crystallization from hexane, 1:100 for −S at 0C and 1:40 for −B at 10C. It is the only form obtained from solvent or melt if 10% or more secondary ester is present. It can be converted to α (without first melting) by warming to 43C in the case of 1-PGMS. Raising the crystallization temp or decreasing the solvent proportions favors Form III over Form I. Mixtures of I and III are commonly obtained. In the 1-PGMB case, pure Form I is stable 1 week at 49C; mixtures of I and III increase in III content under the same conditions.

Nomenclature is a significant concern in this study. For several reasons the authors prefer not to use that of Kuhrt et al (5), except for the form which would be widely recognized as α on the basis of its strong 4.13Å short-spacing. Kuhrt's terms β′ and β suggest a glyceride nomenclature where β′ has commonly signified a form with multiple short-spacings and a main spacing near 4.2Å, and where β has signified a form with strong 4.6Å spacing. Actually, with 1-PGMS there are three forms with multiple short-spacings and a main spacing near 4.2Å, and there is no form with a strong 4.6Å spacing. In the present paper the authors also avoid the term subα, appropriate enough for some technical PGMS phases (10), but subα has been applied in the past to low-temp forms transforming (reversibly) to α, having strongest short-spacing at 4.2Å and additional short-spacing line or lines, and having long-spacing approx equal to α (11); such criteria apply to Form III, but not to Form I. The designations I, II, III of the present paper have distinction as their only important significance. They do happen to represent the order (in time) of first recognition of the three non-α forms. The following Table IV is believed to represent with as much clarity as possible the interrelationship of the present nomenclature with that of Kuhrt et al.

The Polymorphism of 2-PGMS. The stable form of 2-PGMS at lower temps, called Form I and of DCL appears to be continuous with Form I of 1-PGMS and, hence, with the normal form of a wide range of mixed compositions. The somewhat branched molecular configuration of 2-PGMS apparently favors the tilted structure of Form I. Actually, the diffraction pattern of 2-PGMS from solvent remains that of Form I up to 38C and presumably to the melting point at 40.6C. However, Form I of a melted, chilled sample gives way reversibly to α by 38C. By differential thermal analysis (DTA) the behavior is confirmed, Form I from solvent giving a single sharp peak at the melting level, Form I from melt showing a lower peak for transformation to α in addition to the (α) melting peak. The difference in Form I from solvent and melt is presumed to be a matter of crystal size or degree of perfection.

Just under the melting point, the stable form appears to be α of SCL structure contrasting with DCL for Form I and DCL for α of 1-PGMS, but in this SCL feature, at least, like the SCL structure of Form II of 1-PGMS. The α form of 2-PGMS differs further from the α form of 1-PGMS in lacking the weak, minor short-spacing lines in the diffraction pattern of the latter compound.

The transformation Form I (DCL) $\rightleftharpoons \alpha$(SCL) suggests a major shifting of long chains from a head-to-head DCL structure to some form of SCL structure, either head-to-tail or perhaps with pairing of reversed chains. No macroscopic effects correlated with the change have been observed.

The Binary System 2-PGMS—1-PGMS. It became evident early that much of the complexity in phase behavior of propylene glycol monostearate was due to the content of 2-PGMS in the predominant 1-PGMS isomer. A detailed study of the 2-PGMS—1-PGMS system was strongly indicated. The results of such a study are shown in Table III and Figure 2.

At high 2-PGMS levels, α-1 (α of SCL structure) occurs just below the melting point (after chilling the melt); α-2 (α of DCL structure) occurs similarly on the other side of the diagram. The α melting point curve is continuous, with a sharp break near 50%, the existence of a break corresponding to the occurrence of α-1 for 2-PGMS and α-2 for 1-PGMS. The weakness and diffuseness of the long-spacings in the intermediate region do not permit determination by diffraction technique of the range of existence of the two α phases.

TABLE IV

Comparison of Nomenclatures

M & L[a]	K, B & B[b]
I }	β'
III }	
II	β
α	α

[a] Martin and Lutton.
[b] Kuhrt, Broxholm and Blum.

The stable 1-PGMS phase, Form II, shows a sharp drop in mp on 2-PGMS addition; the phase is difficult to obtain even from solvent with a substantial percentage of 2-PGMS.

The room-temp phase (from melt) is Form I up to 80% or 90% 1-PGMS; above 90% Form III appears (although Form I is still obtainable from solvent) and will transform to Form II, but slowly.

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Composition and Structure of Phospholipids in Chicken Muscle Tissues[1, 2]

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Abstract

Lipids extracted from breast muscle and thigh muscle of one-year old chickens on a standard MSU-Z-4 diet have been fractionated by silicic acid column chromatography into nonphospholipids, phosphatidyl ethanolamine, phosphatidyl serine, phosphatidyl choline (lecithin), and sphingomyelins. Phospholipid fractions were identified by thin-layer chromatography and the quantity of each determined by gravimetric analysis, analysis of the phosphorus content, and infrared spectra.

The phospholipid content of thigh muscle (dark meat) lipids was higher than that in the breast muscle (white meat). Phosphatidyl choline and phosphatidyl ethanolamine were found in relatively greater amts than phosphatidyl serine and sphingomyelins. Enzymatic hydrolysis followed by gas-liquid chromatographic analysis of the fatty acids liberated and those in the lysocompounds was used to establish the positional specificity of the fatty acids in the phosphoglycerides. The polyunsaturated fatty acids are located primarily at the β-position and the saturated fatty acids at the α'-position. The qualitative and quantitative determination of the plasmalogens was also accomplished.

[1] Michigan Agriculture Experiment Station Journal Article No. 3527.
[2] Presented at the AOCS Meeting in Chicago, October, 1964.

Introduction

THE PHOSPHOLIPIDS of skeletal muscle have not been studied to the same extent as the phospholipids of organ and neural tissue and those of bacteria. Recent studies on the composition of the phospholipids of avian skeletal muscle have been reported by Davenport (3), and Gray and MacFarlane (5) on pigeon, and by Marion and Woodroof (11) on the broiler. The objective of this study was to investigate the composition and structure of the phospholipids of both dark (thigh) and white (breast) meat in chicken.