Surface Properties of 1,2-Dipalmitoyl-3-acyl-*sn*-glycerols†

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ABSTRACT: Stereospecific 1,2-dipalmitoyl-*sn*-glycerol and a series of 1,2-dipalmitoyl-3-acyl-*sn*-glycerols (TGs) with 3-acyl chains of two through six and eight carbons in length were synthesized. Pressure–area isotherms at 27 °C, surface melting temperatures (T_s), and equilibrium spreading pressures (esp) measured at the bulk melting temperature (T_f) were obtained for each TG and for dipalmitin. Whereas dipalmitin and the 3-acetyl-TG condense directly to an expanded mesomorphous state (30–33 Å^2/palmitoyl chain at the vapor pressure, π_v), the 3-propionyl- through 3-octanoyl-TGs show an area per molecule (in the liquid at π_v) that increases linearly from 105 to 130 Å^2/molecule (slope = 5 Å^2/CH$_2$ group). This slope suggests that the 3-acyl chains are lying flat on the water at the end of the gas–liquid transition. Before solidification at 42–47 Å^2/molecule, the 3-propionyl- through 3-hexanoyl-TGs show a transition corresponding to the immersion of the 3-acyl chain. The pressure at this transition, π_{tr}, vs. 3-acyl carbon number is linear and indicates a chain immersion energy of 497 cal mol^{-1} per CH$_2$. In contrast, the 3-octanoyl chain is not forced into the water but rather is pushed into the monolayer to lie parallel to the palmitoyl chains. As the *sn*-3 chain is lengthened, T_s decreases from 68 to 25 °C, but the 3-octanoyl monolayer does not solidify even at 5 °C because the short upright octanoyl chains fluidize the palmitoyl chains. The esp (at T_f) drops from 31.7 mN m^{-1} for dipalmitin to 20.6 mN m^{-1} for the 3-acetyl-TG. The esp for the 3-octanoyl-TG is 14.8 mN m^{-1}. In summary, increasing the length of the shorter 3-acyl chain of these diacid TGs decreases the T_s and the esp. In monolayers, the shorter 3-acyl chains, lying flat on the surface at π_v, either submerge into the aqueous phase if π_{tr} is less than esp or stand up and fluidize the monolayer if π_{tr} is greater than esp.

Naturally occurring triacylglycerols in both animals and plants are comprised of three fatty acids esterified to glycerol. Most naturally occurring triacylglycerols are asymmetric since the fatty acids esterified at the 1- and 3-positions are different (Kuksis, 1978). The final step in the synthesis of triacylglycerols involves the enzyme diacylglycerol acyltransferase that utilizes activated fatty acid to esterify the *sn*-3 (or *sn*-1) carbon of the glycerol. The preferred substrate is 1,2-diacyl-*sn*-glycerol (O'Doherty, 1978). The fatty acid in the 3-acyl position in most fats and oils is usually a long-chain fatty acid. However, certain plant oils and especially milk triacylglycerols from ruminants are highly enriched with short-chain fatty acids in the 3-position, that is, fatty acids containing eight carbons or less (Breckenridge, 1978; Breckenridge & Kuksis, 1968). In bovine milk triacylglycerols at least 50% of the *sn*-3 positions are esterified with short-chain fatty acids (Breckenridge, 1978).

The utilization of short-chain fatty acids probably arises from the production of many short-chain fatty acids in the rumen which are absorbed, activated, and utilized by the diacylglycerol acyltransferase in the mammary gland. In fact, when linoleic-rich seed oils are coated by formalated casein that is resistant to rumen enzymes and are fed to sheep, the unsaturated seed oil fatty acids are absorbed without being catabolized to the various smaller fatty acids. The bovine milk fat derived from such animals has a large portion of *sn*-3 position preferentially esterified to linoleic acid rather than to short-chain fatty acids (Mills et al., 1976). Even in some nonruminants such as the rat the *sn*-3 position is greatly enriched in short- and medium-chain fatty acids (Staggers et al., 1981; Aw & Grigor, 1980). These shorter chain fatty acids are more easily hydrolyzed by pancreatic lipase (Jensen et al., 1964) and lingual lipase (Staggers et al., 1981; Fernande-Warnakulasuriya et al., 1981; Paltauf et al., 1974).

In an attempt to understand the mechanisms of this preferential hydrolysis of short- and medium-chain fatty acids at the *sn*-3 position, we have synthesized a homologous series of 1,2-dipalmitoyl-3-acyl-*sn*-glycerols with acyl chains varying from two to eight carbons (Kodali et al., 1984). The bulk properties of this series has been examined (Kodali et al., 1984), but because triacylglycerols are hydrolyzed at a triacylglycerol–water interface (Entressangles & Desnuelle, 1968), we have examined the interfacial characteristics of these triacylglycerols. We found them to be a particularly interesting group of molecules in that their physical properties at the interface are dictated by the length of the fatty acyl chain at the *sn*-3 position. The acetyl derivative prefers the aqueous side of the interface and allows the two palmitate chains to solidify at a very low pressure. On the other hand, if the *sn*-3 chain contains eight carbons, the octanoate cannot be forced into water and thus must lie side by side in the monolayer with the two palmitate chains. The presence of the octanoate in the film prevents the crystallization of the palmitate residues and thus fluidizes the film to very low temperatures. If the *sn*-3 acyl group is intermediate in length, having from 3 to 6 carbons in the fatty acid moiety, it can be pushed into the aqueous phase, but this requires increasing energy the longer the chain length. At surface pressures believed to occur in emulsions in stomach or intestinal contents, we suggest that the short-chain fatty acids actually protrude into the aqueous phase, making them more available to enzymatic hydrolysis.

MATERIALS AND METHODS

Stereospecific 1,2-dipalmitoyl-*sn*-glycerol and a series of 1,2-dipalmitoyl-3-acyl-*sn*-glycerols with even carbon saturated fatty acyl chains of two through eight carbons in length were synthesized (Kodali et al., 1984). The triacylglycerols with 3-acyl chains of three and five carbons in length were also

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synthesized. Approximately 5 mg of each lipid was measured to the nearest 0.01 mg and dissolved in 25 mL of high-pressure liquid chromatography (HPLC)[1] grade heptane in a chromic acid rinsed volumetric flask. Care was taken to mark the fluid level on the volumetric flasks so that solvent evaporation during storage could be detected.

Pressure–Area Isotherms. The Langmuir film balance consisted of a Teflon-coated trough 14 cm wide by 70 cm long by 1.6 cm deep. All isotherms were obtained by continuous compression at room temperature (27 ± 0.5 °C). Surface pressures were measured with a 1-cm^2 platinum Wilhelmy plate suspended from a Cahn electrobalance. Isotherms were directly recorded by a Hewlett-Packard X–Y recorder. A Hamilton syringe was used to spread 84 nmol of solute on the surface, and at least 10 min were allowed for the solvent to evaporate before lowering the Wilhelmy plate to the surface and starting compression. Each isotherm was obtained with a freshly prepared film that was compressed at a rate of 53.6 cm^2/min (8.9×10^{15} Å^2/s) [~3.5 Å^2/(chain·min)]. Three isotherms obtained under identical conditions were superimposable to within 1.5 Å^2/molecule. Merck extraclean talc baked at 700 °C was dusted on a portion of the monolayer in order to monitor viscosity by observing talc movement in response to a light jet of air. Solidification of the monolayer indicated by nonmovement of the talc was reproducibly observed to within 1.5 Å^2/molecule. A test for hysteresis and compression rate dependence was carried out for one of the isotherms (PP5). A difference in compression and expansion isotherms at the transition of 0.6 mN m^{-1} and 3 Å^2/molecule was observed. The pressure in the two-phase region decreased by 0.2 mN m^{-1} when the compression was stopped for 5 min. These values indicate that the deviation from equilibrium is small enough to not affect the conclusions of the study.

Surface Melting Temperature and Equilibrium Spreading Pressure. Chromic acid rinsed glass jars 4.5 cm in diameter by 2.5 cm tall were half filled with double-distilled water and equipped with a clean glass thermometer and a magnetic stirring bar. Enough lipid was spread on the surface to make the surface concentration about 1.5 times the amount necessary to cover the entire surface as a monolayer. This ensured that excess lipid was present but not enough to form a thick-multilayered crystal on the surface. Talc was dusted on the solid film in order to monitor viscosity as the entire system was heated and the subphase stirred by a combination magnetic stirrer and hot plate. The temperature at which the surface became fluid was recorded as the surface melting temperatures, T_s. The accuracy was ±1 °C. The equilibrium spreading pressures (esp) were measured at just above (2–4 °C) the bulk melting temperature of each compound. By use of the same apparatus used in the measurement of T_s, several small crystals were placed on the surface and the subphase heated until the crystals melted. Approximately 1 min later the surface tension was measured and then used to calculate the esp. An uncertainty in the esp of ±1.0 mN m^{-1} mainly due to temperature fluctuation was estimated. The effect of temperature on the esp for the 3-octanoyl compound was measured between 30 and 52 °C by attaching a thermocouple, with its junction placed just below the water surface, directly to the X–Y recorder. After calibration, a continuous graph of surface tension vs. temperature was produced by gradually changing the temperature.

Table I: Melting Temperatures and Equilibrium Spreading Pressures (esp) of 1,2-Dipalmitoyl-3-acyl-*sn*-glycerols

3-substituent	T_f[a] (°C)	T_s[b] (°C)	$T_f - T_s$ (°C)	T_α[c] (°C)	esp (mN m^{-1})	T[d]
unsubstituted	68.5	68.5[e]	0	51.0	31.7	70
acetyl	51.0	51.0	0	32.5	20.6	55
propionyl	43.0	47.0	−4.0		16.6	47
butyryl	44.0	41.0	3.0	21.5	16.3	46
pentanoyl	39.2	33.5	5.7		14.1	41
hexanoyl	43.0	25.0	18.0		16.3	46
octanoyl	44.0	<5	>39		14.8	47

[a] Stable bulk melting temperatures. From Kodali et al. (1984). Note the depressed values for the two odd members. [b] Surface melting temperatures. The octanoyl derivative remained as a fluid monolayer down to 5 °C. [c] Melting temperatures of the α-phase. From Kodali et al. (1984). [d] Temperature at which esp was measured; 2–4 °C above T_f in all cases. [e] Error is estimated as ±1.0 °C for T_s and ±1.0 mN m^{-1} for esp.

RESULTS

Surface Melting Temperature and Equilibrium Spreading Pressure. Values of the stable bulk melting temperature, T_f, the surface melting temperature, T_s, and $T_f - T_s$ for each compound are given in Table I. The metastable α-form melting temperatures (T_α) (Kodali et al., 1984) are given for comparison. The T_f values are depressed for the two odd members of the series. A surface melting temperature for the 3-octanoyl compound was not obtained since the monolayer stayed fluid down to 5 °C.

The esp values measured at just above T_f for each compound are also given in Table I. It was shown that spreading pressure rises nonlinearly as the temperature is increased for the 3-octanoyl compound. The spreading pressures were 14.1 mN m^{-1} at 30 °C, 14.3 mN m^{-1} at 40 °C, 14.6 mN m^{-1} at 45 °C, and 15.2 mN m^{-1} at 50 °C.

Pressure–Area Isotherms. Pressure–area isotherms for 1,2-dipalmitoyl-*sn*-glycerol (PPOH) and the 3-acetyl (PP2), 3-propionyl (PP3), 3-butyryl (PP4), 3-pentanoyl (PP5), 3-hexanoyl (PP6) and 3-octanoyl (PP8) compounds are shown in Figure 1. The area per molecule of the liquid phase (A_v) in equilibrium with its gas (i.e., at the vapor pressure, π_v) can be read from the isotherm as the area per molecule at the end of the gas to liquid transition (i.e., at the departure from the base line indicated by the horizontal bars in Figure 1). In all cases A_v was estimated as a range because there was not a sharp break from the base line. PPOH showed a base-line surface pressure of 0.4 mN m^{-1}. A_v was 58–64 Å^2/molecule, and the isotherm rose sharply after 45 Å^2/molecule. Solidification occurred at 44.3 Å^2/molecule at a pressure of 2.3 mN m^{-1}. PP2 showed a base-line surface pressure of 0.45 mN m^{-1}. A_v was 65–70 Å^2/molecule, and the isotherm rose abruptly after 47 Å^2/molecule. Solidification occurred at 45 Å^2/molecule at a pressure of 3.6 mN m^{-1}. PP3 showed a base-line surface pressure of 0.65 mN m^{-1}. A_v was 102–106 Å^2/molecule. The pressure then increased with a discontinuity in the slope at 95 Å^2/molecule at a pressure of 1.3 mN m^{-1}. Solidification occurred at 45 Å^2/molecule at a pressure of 3.8 mN m^{-1}. The isotherm then rose abruptly. PP4 showed a base-line surface pressure of 0.45 mN m^{-1}. A_v was 110–113 Å^2/molecule. The pressure then increased with a discontinuity in the slope at 84.5 Å^2/molecule at a pressure of 5.8 mN m^{-1}.

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[1] Abbreviations: TG, triacylglycerol; HPLC, high-pressure liquid chromatography; T_s, the temperature at which the lipid monolayer becomes fluid; esp, equilibrium spreading pressure, i.e., the surface pressure of the monolayer in equilibrium with the bulk; T_f, the stable bulk melting temperature; T_α, the metastable α-form melting temperature; PPOH, 1,2-dipalmitoyl-*sn*-glycerol; PP2, 1,2-dipalmitoyl-3-acetyl-*sn*-glycerol; PP3, 1,2-dipalmitoyl-3-propionyl-*sn*-glycerol; PP4, 1,2-dipalmitoyl-3-butyryl-*sn*-glycerol; PP5, 1,2-dipalmitoyl-3-pentanoyl-*sn*-glycerol; PP6, 1,2-dipalmitoyl-3-hexanoyl-*sn*-glycerol; PP8, 1,2-dipalmitoyl-3-octanoyl-*sn*-glycerol; A_v, the area per molecule of the liquid monolayer in equilibrium with the gas; π_v, the monolayer vapor pressure.

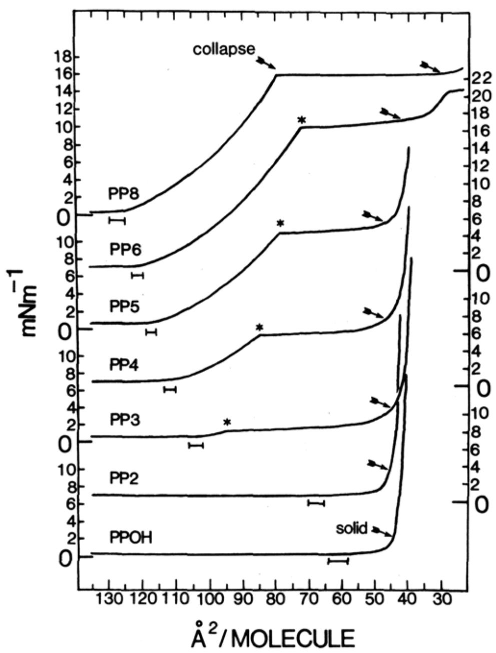

FIGURE 1: Isotherms for the seven compounds at room temperature (27 ± 0.5 °C). The vertical scales for each isotherm are on alternate sides of the graph starting on the left for PPOH. Arrows indicate points of solidification unless otherwise noted. For PPOH through PP6 the area at solidification is 42–47 Å^2/molecule. PP8 solidifies at 30.4 Å^2/molecule. The discontinuities (asterisks) in the isotherms of PP3 through PP6 result from immersion of the 3-acyl chains. The discontinuity in the PP8 isotherm results from monolayer collapse. The approximate area at which the pressure begins to rise from the flat part of the isotherm (horizontal bars) is the area of the liquid phase when it is in equilibrium with the gas phase.

Solidification occurred at 46.8 Å^2/molecule at a pressure of 7.6 mN m^{-1}. PP5 showed a base-line surface pressure of 0.6 mN m^{-1}. A_v was 116–119 Å^2/molecule. The pressure then increased with a discontinuity in the slope at 77.8 Å^2/molecule at a pressure of 10.9 mN m^{-1}. Solidification occurred at 47.2 Å^2/molecule at a pressure of 11.6 mN m^{-1}. PP6 showed a base-line surface pressure of 0.55 mN m^{-1}. A_v was 120–123 Å^2/molecule. The pressure then increased with a discontinuity in the slope at 72.2 Å^2/molecule at a pressure of 16.0 mN m^{-1}. Solidification occurred at 42.2 Å^2/molecule at a pressure of 16.8 mN m^{-1}. PP8 showed a base-line surface pressure of 0.3 mN m^{-1}. A_v was 125–130 Å^2/molecule. The pressure then increased with a sharp break at 79.5 Å^2/molecule at a pressure of 15.5 mN m^{-1}. Further compression produced a perfectly horizontal isotherm down to 39 Å^2/molecule with solidification at 30.4 Å^1/molecule.

DISCUSSION

Pressure–Area Isotherms. PPOH shows a horizontal low-pressure isotherm down to approximately 60 Å^2/molecule with solidification at 44.3 Å^2/molecule. At solidification there are 22 Å^2 per acyl chain, indicating close chain packing. PP2 shows a similar isotherm to that of PPOH with solidification at 45 Å^2/molecule. At solidification there is enough area per molecule for only two acyl chains so that the 3-acetyl chain must be submerged in the water.

Dervichian has classified fatty chain monolayer states according to the area per chain, A_v, at the vapor pressure, π_v (Dervichian, 1954). Briefly, they are liquid (>38 Å^2/chain), expanded mesomorphous (24–33 Å^2/chain), mesomorphous (fluid, 23.5 Å^2/chain), and solid (rigid, 20.5–22 Å^2/chain). For example, tripalmitin at its π_v is liquid above 45 °C, expanded mesomorphous from 40 to 45 °C, and solid below 35 °C. At 27 °C PPOH and PP2 probably condense directly to an expanded mesomorphous state since A_v is 61 (30.5 Å^2/chain) and 67 Å^2/molecule (33.5 Å^2/chain), respectively. However, PP3, with an A_v of 102–106 Å^2/molecule, probably condenses into the liquid state with an area per palmitoyl chain of at least 38 Å^2. This amounts to at least 76 Å^2 for the two palmitoyl chains leaving at most 26–30 Å^2 for the 3-propionyl chain. This area is too large for propionic acid lying flat on the water surface. If the 3-acyl chain is truly lying flat, then the area occupied would be equivalent to the chain length times its width or about 4.5 Å(1.25 Å + 1.25 Å + 1.5 Å) = 18 Å^2. However, if the 3-carbon of the glycerol and the ester group were also in the surface then the area would total about 6.7 Å × 4.5 Å = 30 Å^2 (Figure 2).

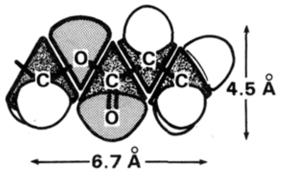

FIGURE 2: Schematic diagram of a 3-propionyl chain lying flat on the water. The total area occupied by the 3-carbon of the glycerol (left), the ester group, and the fatty acid (right) is estimated to be 6.7 Å × 4.5 Å = 30 Å^2.

Assuming that the 3-acyl chains of PP4 through PP8 are also lying flat on the surface in the liquid phase at π_v, then A_v should increase by ~5 Å^2 for each additional carbon in the *sn*-3 chain. In Figure 3a, A_v is plotted vs. 3-acyl carbon number. A line which accommodates ranges of A_v has a slope of ~5 Å^2 per carbon and an intercept at zero carbons of 92 Å^2. This slope is consistent with the suggestion that the *sn*-3 chains of three to eight carbons are lying flat on the surface at the end of the gas–liquid transition.

In contrast to PP8 which solidifies as a bilayer at 30.4 Å^2/molecule, PP3 through PP6 solidify between 42 and 47 Å^2/molecule, indicating that only two and not three chains are solidifying as a monolayer. The shorter *sn*-3 chains of PP3 through PP6 must be submerged in the subphase at solidification. Since the *sn*-3 chains are not submerged in the liquid state at π_v, they must be forced into the water at some point during compression of the liquid. PP3 through PP6 have discontinuities in their isotherms at 95.0, 84.5, 77.8, and 72.2 Å^2/molecule, respectively (at asterisk in Figure 1), indicating phase transitions. One phase consists of the triacylglycerol with all three chains out of the water and the other phase consists of the triacylglycerol with the shorter *sn*-3 chain and the *sn*-3 glycerol carbon submerged in the water. As the film is compressed in this two-phase region, the *sn*-3 chains are pushed into the water. After all the *sn*-3 chains are pushed into the water, further compression of the palmitoyl chains solidifies them at 42–47 Å^2/molecule. The pressures at the start of the two-phase regions (discontinuitues) vs. 3-acyl carbon number is linear with a slope of 4.9 mN m^{-1} per carbon (Figure 3b). Note that the PP8 discontinuity pressure does not fall on this line, suggesting that monolayer collapse rather than *sn*-3 chain immersion is occurring.

Dividing the surface pressure by the surface concentration at the two-phase initiation area (at asterisk in Figure 1) yields the energy per mole of monolayer at the transition. A plot of this energy vs. 3-acyl carbon number (Figure 3c) is linear with a slope of 497 cal mol^{-1} per carbon and a *y* intercept of −1298 cal. The 497 cal mol^{-1} per carbon slope represents the surface energy ($\mu_{\text{water}} - \mu_{\text{surface}}$) necessary for chain immersion per additional carbon in the *sn*-3 chain. This energy is only about 56% of the 884 cal mol^{-1} per carbon for transfer of a hydrocarbon chain from a hydrocarbon environment to a water

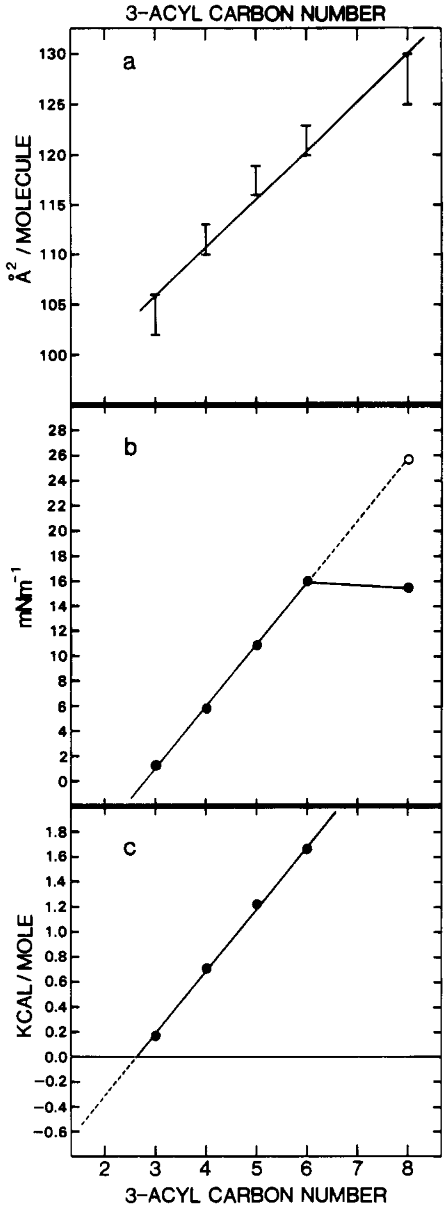

FIGURE 3: (a) Area per molecule of the liquid phase in equilibrium with its gas phase, A_v, vs. 3-acyl carbon number. Since there was not a sharp break from the base line, this area was estimated as a range. The values are given in the text. A line that accommodates all the ranges has a slope of 5 Å^2/molecule per carbon. (b) Pressure at the discontinuity vs. 3-acyl carbon number for PP3 through PP8. The graph is linear for PP3 through PP6 with a slope of 4.9 mN m^{-1} per carbon. The dotted line is an extrapolation. The actual pressure for PP8 does not fall on a line with the others because monolayer collapse and not chain immersion occurs at 15.5 mN m^{-1}. (c) Surface energy needed for 3-acyl chain immersion vs. 3-acyl carbon number. The graph is nearly linear with a best fit slope of 497 cal mol^{-1} per carbon and a y intercept of −1298 cal.

environment at 25 °C (McAuliffe, 1966). This may be due to the chain initially lying flat on the surface being about 50% hydrated with only the upper exposed surface needing transfer to water. Extrapolation of the graph in Figure 3c to two carbons gives a negative value for $\mu_{\text{water}} - \mu_{\text{surface}}$, indicating that it is energetically favorable for the 3-acetyl chain to be submerged in the water at 27 °C even at low surface pressures.

The PP8 isotherm showed a discontinuity at 79.5 Å^2/molecule (26.5 Å^2/chain) at a pressure of 15.5 mN m^{-1}. Extrapolation of the chain immersion pressures to eight carbons (open circle, Figure 3b) yields a chain immersion pressure for PP8 of 25.7 mN m^{-1}. Since the esp of PP8 is estimated to be 14 mN m^{-1} at 27 °C (from the temperature dependence studies), monolayer collapse must occur well before reaching the pressure necessary to immerse the 3-octanoyl chain. The horizontal portion of the PP8 isotherm corresponds to the transition of a monolayer to a bilayer with solidification of the bilayer at 30.4 Å^2/molecule (20 Å^2/chain).

Surface Melting Temperature and Equilibrium Spreading Pressure. Changes in the value of $T_f - T_s$ from one compound to the next must depend on differences in the amount and stability of chain–chain interactions in the solid bulk phase and in the solid monolayer. General packing properties in the bulk state for this series are known (Kodali et al., 1984). Briefly, the stable bulk phase packing arrangements consist of the double-layer diacylglycerol type for PPOH, PP2, and PP4 and a trilayer with the shorter *sn*-3 chains segregated from the palmitoyl chains for PP6 and PP8. The general packing properties of the solid monolayer deduced from the isotherms consist of solidified palmitoyl chains for PPOH and 3-acyl chains immersed in the water with solidified palmitoyl chains on the surface for PP2 through PP6. PP8 does not solidify as a monolayer even at 5 °C because the 3-octanoyl chain cannot be immersed and must mix with and therefore fluidize the palmitoyl chains.

PPOH has nearly identical surface and bulk melting temperatures (Table I) because the extent of palmitoyl chain–chain interaction is similar in the double layer bulk phase and in the monolayer. The hydroxyl group may experience similar hydrogen bonding in the bulk (with neighboring carbonyls) and in the monolayer (with water). PPOH has a high esp of 31.7 mN m^{-1} probably due to the high affinity of the hydroxyl group for the water. In contrast, PP2 has an esp of only 20.6 mN m^{-1}. The added acetyl group causes a large drop in the esp whereas each additional carbon in the *sn*-3 chain causes a much smaller reduction. The loss of the hydroxyl has little or no effect on the stability of the solid palmitoyl chains since $T_f - T_s$ for PP2 is near zero. In the PP2 through PP6 series increasing *sn*-3 chain length coincides with a smoothly decreasing value of T_s. Since the *sn*-3 chains are in the water, as this chain is lengthened there is increasing palmitoyl chain destabilization and a decreasing T_s. Note that T_f is depressed for PP3 and PP5 and that for PP3 T_s is actually greater than T_f. The fact that T_f and T_s are much higher than the melting temperature of hexagonally packed chains (T_α) may indicate a specific chain packing on the surface monolayer like that in the stable bulk phase.

In summary three categories of these triacylglycerols defined by the behavior of the shorter acyl chains during compression of the triacylglycerol monolayers are schematized in Figure 4. Dipalmitin and triacylglycerols with 3-acyl chains of two or less carbons are always hydrophilic at the *sn*-3 position (Figure 4, top). 3-Acyl chains of three to six carbons in length lie flat on the surface of the water at low surface pressure but can be completely hydrated at the *sn*-3 position when the triacylglycerol monolayer is compressed (Figure 4, middle). If the 3-acyl chain contains eight carbons (and probably seven, nine, and ten), the chain cannot be submerged at monolayer surface pressures and is pushed up into the palmitoyl chain phase preventing monolayer solidification (Figure 4, bottom).

Triacylglycerols with short *sn*-3 chains are found in nature with bovine milk butterfat containing a large percentage of butyric acid in the 3-position (Breckenridge & Kuksis, 1968; Pitas et al., 1967). In rats, lingual lipase preferentially hydrolyzes the shorter *sn*-3 chain from rat milk triacylglycerols (Staggers et al., 1981). Pancreatic lipase is specific for hydrolysis of acyl chains from the primary positions of glycerol.

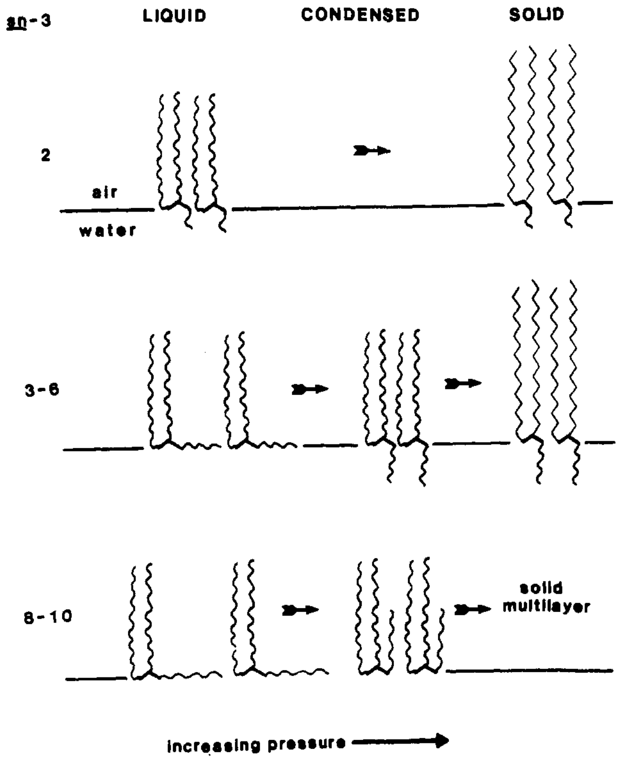

FIGURE 4: Summary diagram of three categories of 3-acyl chain behavior during triacylglycerol monolayer compression. Top: 3-acyl chains are completely submerged regardless of surface pressure. Includes chains with two carbons or less and the hydroxyl group of dipalmitin. Middle: 3-acyl chains lie flat on the water surface at low pressures but are completely submerged at high pressures. Includes chains of three to six carbons. Bottom: 3-acyl chains cannot be submerged at monolayer pressures and therefore prevent monolayer solidification. Includes chains with eight and probably seven, nine, and ten carbons.

The efficiency and specificity of enzymes like lingual lipase and pancreatic lipase may be related to the availability of the 3-acyl chain to the aqueous side of an oil/water interface.

Fluidization of a lipid bilayer is caused by chain unsaturation, cholesterol, or other fluidizing components. The concept that large differences in chain length can also fluidize a monolayer (or bilayer) has been demonstrated in this study.

ACKNOWLEDGMENTS

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Registry No. PPOH, 30334-71-5; PP2, 92734-29-7; PP3, 102871-10-3; PP4, 92841-82-2; PP5, 102871-11-4; PP6, 92841-83-3; PP8, 92734-30-0.

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