Monoacylglycerols alter the lipid composition and molecular mobility of phosphatidylcholine bilayers: ^{13}C NMR evidence of dynamic lipid remodeling

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Abstract The physical effects of monoacylglycerols (MAG) in small unilamellar vesicles composed of phosphatidylcholine (PC), triolein, cholesterol, and varying amounts of monopalmitin and monoolein were studied by ^{13}C-NMR. The signal to noise ratio of the carbonyls of PC and triolein were enhanced by the addition of 1,2-di-[1-^{13}C]palmitoylphosphatidylcholine and tri-[1-^{13}C]oleoylglycerol. The linewidths of the carbonyl- ^{13}C, choline methyl, olefinic carbon, and terminal methyl resonances were measured digitally from vesicles with 0 to 42 mol % of MAG. Significant increases in the linewidth of carbonyl ($P < 0.05$), olefinic and terminal methyl carbons ($P < 0.01$) of vesicles containing 42 mol % monopalmitin indicated that these groups experienced restricted molecular mobility at high monopalmitin concentrations. However, more striking was the apparent displacement of triolein from the surface environment of PC bilayers to an oil-like environment in systems containing only 8 mol % monopalmitin. Displacement of triolein from the surface by monoolein occurred only above 15 mol %. Thus, saturated and monounsaturated monoacylglycerols, natural products of lipoprotein metabolism, dynamically alter both the lipid composition and molecular mobility of lipoprotein surfaces in distinct ways.—**Boyle, E., D. M. Small, D. Gantz, J. A. Hamilton, and J. B. German.** Monoacylglycerols alter the lipid composition and molecular mobility of phosphatidylcholine bilayers: ^{13}C NMR evidence of dynamic lipid remodeling. *J. Lipid Res.* 1996. **37:** 764–772.

Supplementary key words monopalmitin • monoolein • ^{13}C NMR • remnant uptake • lipoprotein lipase

Monoacylglycerols (MAG) are major intermediates in fat metabolism. 2-Monoacylglycerols (2-MAG), along with fatty acids, are produced by acyl position-specific triacylglycerol hydrolases during both the absorption of fat and the metabolism of triglyceride-rich lipoprotein particles. The primary form of dietary fat, triglyceride, is hydrolyzed at the 1- and 3-ester linkages of the glycerol backbone to yield fatty acids and 2-MAG by a combination of gastric and pancreatic lipases (reviewed in ref. 1). Diglycerides are also substrates for the hydrolases, and the end products of lipolysis are 2-MAG and fatty acids. During fat absorption, most of the 2-MAG produced are subsequently used as substrates for the resynthesis of triglyceride (2). The resynthesis takes place in the enterocytes, where the triglyceride is then packaged into chylomicra for transport to the circulatory system (1, 3).

During chylomicron metabolism, the triglyceride is hydrolyzed to fatty acids and 2-MAG by the action of lipoprotein lipase (LPL). The fate of the 2-MAG produced during the lipolysis of triglyceride-rich lipoprotein particles is not well defined. Data support several possible endpoints for these 2-MAG. The MAG may be transported to endothelial cells where they are hydrolyzed to fatty acid and glycerol by monoacylglycerol hydrolase (4). They may remain in the surface of the partially hydrolyzed chylomicra and be transported to the liver to serve as a substrate for either monoacylglycerol acyltransferase or monoacylglycerol hydrolase (5). Studies have also indicated that MAG arising from the action of LPL may be found in either low or high density lipoproteins (LDL or HDL) and be taken up by the liver (6). Regardless of their end point, MAG are a major component of chylomicra particles for a finite period of time and may play a key role in subsequent particle metabolism. The accumulation of MAG in chylomicra remnants is dependent on the amount of serum albumin present, the rate of acyl migration from 2-MAG

Abbreviations: MAG, monoacylglycerols; SUV, small unilamellar vesicles; PC, phosphatidylcholine; LPL, lipoprotein lipase.

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to 1(3)-MAG (a slow process), and the rate of uptake by the liver (5–7). In the capillaries, where active lipolysis occurs, there are necessarily no in vivo measurements of remnant composition or MAG accumulation. However, calculations based on data from in vitro production of chylomicron remnants using bovine LPL show that up to 25 mol % of the total starting triacylglycerol is present as MAG within a few minutes of the start of lipolysis (5–7). As MAG partitions exclusively to the surface, it could readily approach and surpass 40 mol % of surface lipids (5, 7). In fact, the composition of rhesus chylomicron remnants of different sizes collected after limited lipolysis shows that 8.5–25% of the remnant neutral acylglycerols was MAG (5). The ratio of the major surface lipid, phospholipid, to MAG in these preparations was as low as 1:2, illustrating just how enriched in MAG the surface can become during hydrolysis.

For a better understanding of the role that MAG play in lipoprotein metabolism, their physical behavior in chylomicra needs to be defined. Although the surface and core regions of chylomicra are physically and chemically separate, certain molecules may dynamically exchange between them. The surface must be considered the more biologically active portion of the chylomicron because all interactions of the particle with other macromolecules occur at the interface between the surface and the aqueous medium. Therefore, reactions involving lipoprotein particles, such as hydrolysis by LPL, need to be addressed in terms of where the substrates and products are located and how their varying proportions may affect their physical environment.

MAG are surface-active molecules. In an emulsion environment similar to the composition of chylomicra, they would be predicted to partition to the interface between oil and water. In vivo, MAG produced by the action of LPL should be found in the surface of chylomicra where they might also be important mediators in subsequent particle metabolism. A number of studies have implied that the presence of MAG in lipoprotein particles may alter the macromolecular interactions of the lipoprotein particle with enzymes and or apoproteins, thus affecting particle metabolism (8–11). Redgrave, Kodali, and Small (8) proposed that observed differences in chylomicron metabolism may be due to the accumulation of saturated as opposed to unsaturated MAG at the particle surface.

The observed alterations in biological interactions of lipoprotein particles appear to be related to the presence of and chemical type of MAG, but the mechanism of the alterations remains unknown. Many of the previous studies suggest that MAG physically alter the

TABLE 1. Composition of vesicles

Component	Control	MP	MP	MP	MP	MO	MO
				weight %			
EYPC	90	86	82	75	65	82	65
DPPC ^{13}C	2	2	2	2	2	2	2
Triolein ^{13}C	3	3	3	3	3	3	3
Cholesterol	5	5	5	5	5	5	5
Monopalmitin		4	8	15	25		
Monoolein						8	25
				mol %			
EYPC	86.12	78.37	71.33	60.44	47.39	72.18	48.89
DPPC ^{13}C	1.99	1.89	1.81	1.67	1.51	1.83	1.56
Triolein ^{13}C	2.47	2.35	2.25	2.08	1.88	2.27	1.94
Cholesterol	9.43	8.98	8.57	7.94	7.18	8.67	7.41
Monopalmitin		8.40	16.05	27.87	42.03		
Monoolein						15.05	40.19
Molar ratios							
PC/MP		9.33	4.45	2.17	1.13		
PC/MO						4.80	1.22
Triolein/MP		0.28	0.14	0.07	0.04		
Triolein/MO						0.15	0.05

EYPC, egg yolk phosphatidylcholine; MP, monopalmitin; MO, monoolein.

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surface membrane in some manner that changes the association of enzymes and/or cofactors with the particle surface. However, no data have been published addressing the physical effects of MAG in lipoprotein membranes. While little is known of the effect of MAG on the surface properties, it is known that changing the surface properties from solid to viscous to fluid by changing the phospholipid acyl chains and by adding cholesterol have major effects on protein binding to the surface and particle metabolism (12, 13). Therefore, this study was designed to investigate directly the physical effects of MAG in membranes using nuclear magnetic resonance (NMR).

To investigate the physical effects of MAG in model biological membranes, small unilamellar vesicles (SUV) composed of egg yolk phosphatidylcholine (PC), 1,2-di-[1-^{13}C]palmitoylphosphatidylcholine (^{13}C-PC), tri-[1-^{13}C]oleoylglycerol (^{13}C-TO), cholesterol, and varying amounts of monopalmitin and monoolein were prepared. The vesicle composition was designed specifically to mimic the surface composition of triglyceride-rich lipoprotein particles used in previous studies (8–11). Specifically, excess ^{13}C-TO was added to insure saturation of the monolayers of the vesicles with ^{13}C-TO and to show some excess ^{13}C-TO present in an oil phase (14). This excess oil phase TO has been shown to separate from vesicles in small emulsion particles (14–17). The triglyceride (^{13}C-TO)-saturated vesicle monolayers serve as models for the monolayers of chylomicra and the ^{13}C-TO present in an oil phase monitors the shift of triglyceride from surface monolayer to chylomicron oily core (18). Of prime interest was the surface environment of triglyceride-rich lipoprotein particles and what physical differences occur upon incorporation of MAG.

TABLE 2. Vesicle size

Sample	Size
	nm
Control	21.9 ± 7.4
8 mol % Monopalmitin	21.6 ± 4.2
16 mol % Monopalmitin	26.8 ± 5.6
27 mol % Monopalmitin	41.9 ± 6.1[a]
42 mol % Monopalmitin	34.9 ± 5.4[b]
15 mol % Monoolein	18.2 ± 5.6
40 mol % Monoolein	39.6 ± 6.1[a]

Values are given as the mean vesicle diameter ± one standard deviation as measured by negative staining electron microscopy. Size distributions were analyzed by Student's *t*-test.

[a]Vesicle size distribution differs significantly from control, $P < 0.01$.

[b]Vesicle size distribution differs significantly from control, $P < 0.05$.

The signal to noise of the carbonyls of PC and triolein were enhanced by the addition of ^{13}C-labeled PC and TO.

The linewidths of well-resolved resonances corresponding to carbons of the choline headgroup, carbonyl groups, olefinic groups, and terminal methyl groups were used to estimate the transverse relaxation (T^*_2) time of specific carbons throughout the lipid surface. The effects of MAG on the mobility of membrane components were then compared. It was speculated that the incorporation of saturated monopalmitin into phospholipid membranes might restrict the mobility of the acyl chains while incorporation of monoolein might do the opposite.

METHODS AND MATERIALS

Egg yolk phosphatidylcholine was obtained from Avanti Polar Lipids, Birmingham, AL; cholesterol from Nu-Chek Prep, Elysian, MN; tri-[1-^{13}C]oleoylglycerol from Cambridge Isotope Labs, Cambridge, MA; 1,2-di-[1-^{13}C]palmitoylphosphatidylcholine from Serdary Research Labs, London, Ontario; 1-monopalmitin from Hormel Institute, and 1-monoolein from Sigma, St. Louis, MO.

Vesicle preparation

Vesicles were prepared by dispensing a total of 100 mg of lipids from stock solutions of chloroform–methanol 2:1 into small glass test tubes; see **Table 1** for compositions. Organic solvent was evaporated under N_2. The dry lipid film was dispersed in 1.8 ml of 0.05 M Tris buffer (pH 7.4 at 37°C) containing 0.16 M KCl and sonicated under N_2 for 45–50 min using a pulsed mode sonifier from Heat Systems Co. (Melville, NY) at 60 Watts. Sonication was performed in a cold room, approximately 4°C. After sonication, test tubes were centrifuged for 5 min on a labtop centrifuge to remove fragments of the sonicator tip, and vesicles were transferred to 10-mm NMR tubes. To each NMR tube was added 0.20 ml of 99.9% D_2O to make a total volume of 2.0 ml with a lipid concentration of 50 mg/ml.

Vesicle sizing

All vesicle preparations were sized using negative stain electron microscopy (19). A small aliquot of each suspension was diluted 1:300 with pure water and immediately placed on a freshly glow-discharged carbon, formvar-coated grid, blotted, stained with 1% sodium phosphotungstate (pH 7.4), blotted, and air dried.

Control vesicles were vitrified for morphological observation and sizing. Vesicles were diluted 1:10 or 1:50 with pure water, applied to hydrophilic holey carbon,

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formvar-coated grids, blotted on two sides with filter paper, and immediately plunged into liquid ethane cooled to liquid N_2 temperature (~ -180°C). Vitrified samples were maintained at -172°C in a Gatan Cooling Holder while photographed under low dose conditions in a Philips CM12 transmission electron microscope.

^{13}C NMR

^{13}C NMR spectra were obtained at 50.3 MHz with broad band decoupling, a 90° pulse width of 12.2 μs, spectral width of ± 10,000 Hz, block size of 16 K data points, 4000–7000 acquisitions at 37°C using a Bruker WP 200 spectrometer (14). Spin lattice relaxation times (T_1) were measured as in (14), by using inversion recovery, on control and 42 mol % monopalmitin vesicles. Carbonyl, olefinic, and choline methyl groups had T_1 values of 2.1 sec, 0.7 sec, and 0.7 sec, respectively, for both control and monopalmitin vesicles. The terminal methyl carbon had a T_1 of 2.8 sec in control and 2.1 sec in monopalmitin vesicles. A pulse delay of 7.6 sec was used to give a total repetition rate of 8.4 sec (~$4 \times T_1$) for data acquisition as described previously (20, 21). As found previously (14), carbonyls of both PC and triolein exhibited T_1s of ~2.1 sec. ^2H_2O was used for internal shim and lock signal. Spectra were processed with automatic baseline correction and 1.0 Hz line broadening. Chemical shift assignments were referenced to the terminal methyl carbons at 14.1 ppm (14). Linewidths ($\Delta \nu_{1/2}$) were measured digitally and T^*_2 was calculated from $*T = 1/\pi \Delta \nu_{1/2}$.

RESULTS AND DISCUSSION

Vesicle size

The main objective was to investigate the physical effects of MAG in bilayers containing cholesterol and saturating amounts of triolein (14, 17) as models for chylomicron and remnant surfaces (16, 18–23). It was important to determine whether the addition of MAG significantly altered the size of vesicles, as size may affect the interpretation of NMR results. The mean diameters of vesicles (**Table 2,** obtained by negative staining electron microscopy) containing 27 and 42 mol % MAG were larger than control vesicles, $P < 0.01$ and $P < 0.05$ respectively. However, the size distributions of vesicles containing less than 27 mol % monopalmitin, (mean ± SD) were not significantly different to controls. Vesicles containing 40 mol % monoolein were significantly larger than control vesicles, $P < 0.01$, while vesicles containing only 15 mol % showed no significant difference in size from the control. In concentrations greater than 15 mol %, monoolein may also be acting as a fusogenic agent, which would yield larger vesicle diameters.

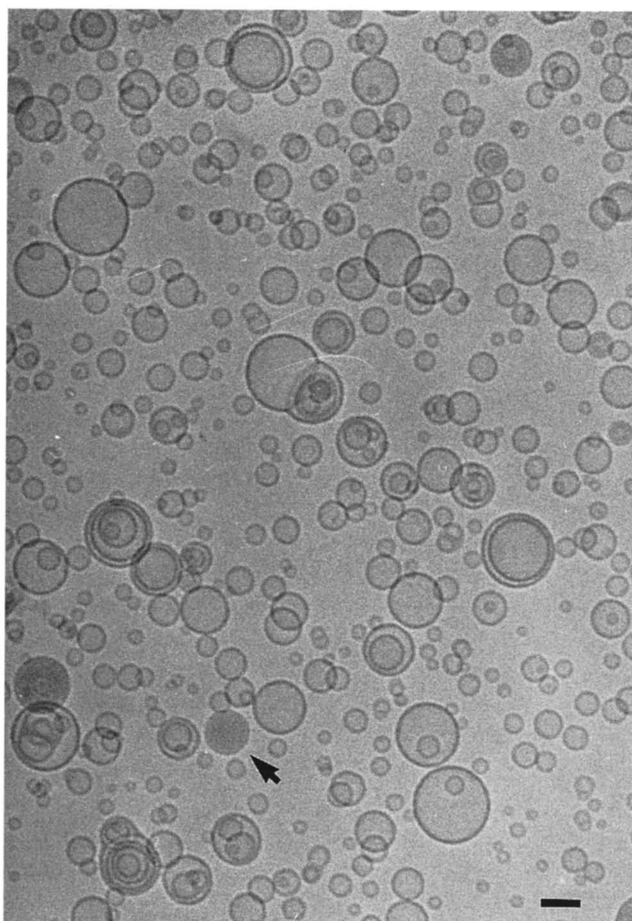

Fig. 1. Cryo-transmission electron micrograph of control phospholipid vesicles, containing 90% EYPC, 5% cholesterol, and 5% triolein by weight to illustrate vesicle morphology. In this and other fields most of the vesicles are unilamellar, ranging from 15 to 70 nm in diameter with a mean diameter of 29.1 ± 15.4 nm. A few of the larger vesicles up to 100 nm contain two or more bilayers. Because of non-homogeneous distribution of particles (see text) mean values obtained in vitreous ice are subject to potentially large errors. The particle marked with the arrow is a microemulsion particle with a core of triolein. A few such particles would be expected from the composition as the maximum solubility of triolein in bilayers of this composition is about 2–2.5 weight percent (17). These particles give rise to the TO_o signals noted by NMR. Bar = 50 nm.

The morphology of control vesicles was investigated using vitreous ice electron microscopy (**Fig. 1**). This preparative technique revealed a heterogeneous population (mean diameter 29.1 ± 15.4 nm) containing predominately unilamellar vesicles, an occasional multilamellar vesicle, and a few particles with triolein cores (arrow). The sizing of vesicles in vitreous ice can be misleading because chosen areas may not be representative. Larger vesicles tend to migrate toward hole edges as the fluid layer is thicker at the hole edge. Small vesicles concentrate in the thinner hole center region. In addition, large vesicles may be squeezed/flattened in

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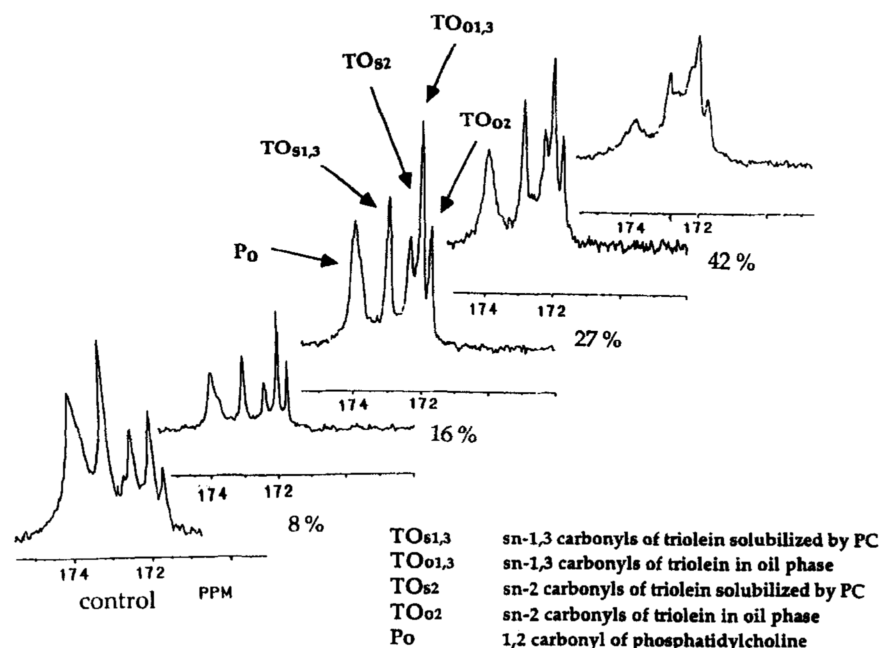

Fig. 2. Expanded carbonyl region of ^{13}C NMR spectra of control phospholipid vesicles left and vesicles with monopalmitin increasing from 8 to 42 mol % right. See Table 1 for actual composition.

regions of thin ice. Determination of the size of the control population by negative staining indicates greater homogeneity (mean diameter 21.9 ± 7.4 nm).

^{13}C NMR

NMR is a non-invasive technique that has been used to study the composition, mobility, and dynamics of model lipid membranes and lipoproteins (14, 16, 20). ^{13}C NMR studies of lipoproteins, bilayer membranes, and albumin in aqueous environment have defined the chemical shift of fatty acids in the different compartments and shown how the distribution of fatty acid changes with external pH (22, 23). The presence of triolein and cholesteryl ester (14, 15, 21) in membranes and the effect of cholesterol decreasing their solubility has also been demonstrated (17, 19, 24). The incorporation of diacylglycerols, their interfacial conformation and transbilayer diffusion rate have also been measured (25).

The relaxation behavior of nuclear spins is dependent on both the chemical and physical environment of the spins. The relaxation time, T^*_2, may be used to describe membrane dynamics. T^*_2 is an approximation of the true spin-spin relaxation time, T_2. While T_2 is technically more difficult to measure in multi-resonance samples, T^*_2 may be determined by measurement of the linewidth at half height from simple one-pulse experiments. This simplification results in contributions to T^*_2 from relaxation mechanisms other than molecular motion. However, studies of many phospholipid membrane environments have shown that the linewidth of ^{13}C resonances and the corresponding T^*_2 are consistently responsive to changes in the mobility of the molecular environment (26–29).

Analysis of the carbonyl region of ^{13}C NMR spectra of vesicles with increasing monopalmitin content shown in **Fig. 2** clearly revealed two distinct physical alterations in the membranes containing MAG relative to control. The linewidth of resonances increased as monopalmitin content increased, especially at concentrations of 42 mol % (**Table 3**). The intensity of triolein carbonyl peaks in the oil phase increased and the triolein carbonyl peaks solubilized in PC (TO_s) decreased with the addition of monopalmitin, indicating that monopalmitin was displacing triolein from the membrane interface. The important intensity shift occurs between 0 (control) and 8% monopalmitin (Fig. 2). A similar displacement of triolein occurred with the addition of monoolein to vesicles as shown in **Fig. 3** but the major shift occurs at higher MAG concentration, between 15 and 40% monoolein (Fig. 3). Also noted was a small decrease in the linewidth of olefinic and terminal methyl carbons with the addition of monoolein, which would indicate an increase in the mobility of these groups with the addition of monoolein.

T^*_2 values calculated from linewidths in the present study were similar to values previously published for PC bilayers (14, 19, 26, 29–31). Broadening of linewidths in NMR spectra may be the result of several factors: increased field inhomogeneity, chemical exchange, chemi-

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TABLE 3. Linewidths of ^{13}C resonances

Sample	EYPC Carbonyl	Olefinic	Choline-CH_3	Terminal-CH_3
		hertz		
Control	24.6 ± 6.4	39.1 ± 1.8	15.3 ± 1.5	10.8 ± 2.5
Monopalmitin				
8 mol %	25.6 ± 4.4	38.3 ± 2.7	14.7 ± 2.0	10.2 ± 1.8
16 mol %	26.2 ± 2.5	51.3	21.4 ± 13.0	10.9 ± 3.5
27 mol %	21.1 ± 1.1	36.3 ± 5.2	13.7 ± 1.2	9.7 ± 0.1
42 mol %;	37.2 ± 4.4[a]	53.2 ± 5.9[b]	15.9 ± 0.1	20.3 ± 1.1[b]
Monoolein				
15 mol %	24.5	34.2	15.9	9.5
40 mol %	19.0	30.6	12.2	8.4

Values of the linewidths of the designated carbon resonances from ^{13}C NMR spectrum of phospholipid vesicles with increasing concentrations of monoacylglycerols are given in hertz, mean ± SD.

[a]Values differ significantly from control, $P < 0.05$, Student's *t*-test.

[b]Values differ significantly from control, $P < 0.01$, Student's *t*-test.

cal shift non-equivalence, or a decrease in the molecular correlation time, τ_c (29, 32). The molecular correlation time, τ_c, is a measure of molecular motion (33) and is directly proportional to viscosity and inversely proportional to diffusivity. The relaxation behavior of nuclei is dependent on molecular motion; in solution T^*_2 is inversely related to τ_c (33). Based on these relationships, if the linewidth of a resonance increases, T^*_2 decreases and τ_c must increase. This indicates that the local physical environment that defines τ_c has changed such that the molecule is more restricted in molecular mobility.

As noted by Spooner et al. (19), vesicles with greater diameters may show increased linebroadening due to the reduced surface curvature which could result in a more rigid packing of fatty acyl chains in bilayers (34). If reduced surface curvature were the predominant cause of linebroadening in these vesicles, then the largest vesicle size distributions would be expected to show the greatest linebroadening. However, the results of the present study indicated that although the 27 mol % monopalmitin sample had significantly larger vesicle diameters than the control and a slightly larger mean vesicle diameter than 42 mol % monopalmitin, linewidths were not significantly greater than control and they were less than the 42 mol % monopalmitin vesicles. Also, samples with 40 mol % monoolein, which had the largest vesicle diameters, did not show increased linebroadening compared to control; rather, the linewidths appeared to decrease. Therefore, in this study, changes in linewidths are attributed to specific effects from the accumulation of monoacylglycerols in the bilayer and not to changes in vesicle size.

The carbonyl region of ^{13}C spectra of vesicles containing monopalmitin displayed a significant increase in linewidth at 42 mol %, $P < 0.05$, as seen in Fig. 2. The choline carbons showed no significant changes in linewidth with monopalmitin content, and the acyl chain regions monitored by terminal methyl and olefinic carbons showed little change between 0 and 27 mol % (Table 3). At 42 mol % monopalmitin, olefinic and terminal methyl linewidths were significantly greater than controls, $P < 0.01$, indicating more restricted motion in the acyl chains. This indicates that almost all portions of the PC bilayer excepting the choline groups were affected by high incorporation of monopalmitin.

Unlike monopalmitin, monoolein caused an apparent decrease in linewidth of olefinic and terminal methyl carbons (Table 3). Monoolein contains one *cis* double bond between carbons nine and ten. This introduces a kink in the hydrocarbon chain. When aligned in the bilayer, the double bond of monoolein would be about halfway down the chain or approximately in the same location as the double bonds from the *sn*-2 unsaturated acyl chains of egg PC as well as the unsaturated groups of triolein. Increasing the number of kinks in the inner space of the bilayer might create more free volume in the region of both the olefinic and terminal methyl carbons. More free volume would allow more space for molecular motion and as a consequence τ_c and linewidth would decrease (T^*_2 would increase). A similar increase in T^*_2 was noted in investigations of liver triglycerides in vivo comparing the relaxation times of liver lipids in the fed and fasted state (35). In the fasted state there was a significant increase in the amount of unsaturation with a corresponding increase in T^*_2.

Displacement of triolein from the surface

Triolein is soluble in pure egg PC bilayers up to approximately 2.8 mol % (14, 15, 17, 18). In the present study, both monopalmitin and monoolein displaced

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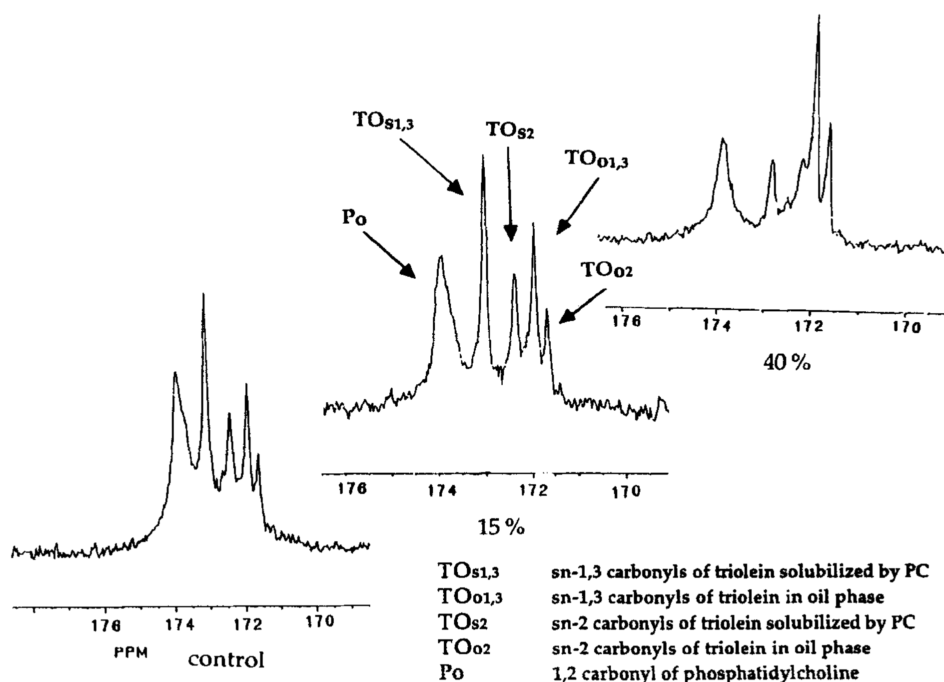

Fig. 3. Expanded carbonyl region of ^{13}C NMR spectra of phospholipid vesicles with increasing mol % of monoolein.

triolein from the surface. The displacement of triolein can be seen in the carbonyl region of the NMR spectra; however, a quantitative integration of these peaks was not possible due to overlap of the signals. Peaks at 173.05 ($TO_{S1,3}$) and 172.38 (TO_{S2}) ppm reflect the carbonyl groups of triolein solubilized in the egg PC bilayer. Peaks at 171.88 ($TO_{O1,3}$) and 171.60 (TO_{O2}) ppm are the carbonyl groups of triolein in an oil phase (14). As the concentration of MAG in the vesicle was increased, the intensity of the triolein oil phase peaks increased while the intensity of the triolein surface peaks decreased (compare 0 and 8% in Fig. 2). The shift in signal intensities between surface and oil phase triolein indicated that the concentration of triolein in the surface decreased with the incorporation of MAG. The increase in oil phase peaks indicates that TO was displaced from the surface into the oil phase. The finite solubility of triglyceride in the membrane surface is dependent on the surface composition and is decreased by cholesterol (17, 18). MAG are direct products of lipolysis of triglyceride-rich lipoprotein particles, while cholesterol is not. The addition of MAG to the surface membrane of lipoprotein particles is thus an immediate consequence of lipolysis. The data show that MAG displace triglycerides from the membrane surface to the oil phase. Thus, as MAG are generated at the interface of lipoproteins MAG may force surface-located triglyceride into the core of the lipoprotein. Evidence that MAG can displace triglyceride from an air/water interface has previously been shown (36). Using a monolayer system on a partitioned trough, Scow, Desnuelle, and Verger (36) determined that lipolytic products formed by LPL immediately locate and spread at the interface. In the presence of lipolytic products, substances with lower spreading pressures such as triglycerides are displaced from the interface.

Conclusions

The addition of MAG to phospholipid vesicles that model the surface of partially hydrolyzed triglyceride-rich lipoprotein particles altered the physical properties of the membrane. Saturated (monopalmitin) and unsaturated (monoolein) MAG exhibited different effects. Monopalmitin restricted the mobility of the carbonyl, olefinic, and terminal methyl carbons when incorporated at 42 mol %. Monoolein at 40 mol % showed little effect on the carbonyl groups but perhaps increased the mobility of olefinic carbons and terminal methyls. Each monoacylglycerol displaced triglyceride from the surface upon addition to vesicles, but monopalmitin produced major effects at 8% while monoolein only produced effects at greater than 15%.

Both the altered molecular mobility and displacement of triglyceride from the surface may be key events in lipoprotein metabolism. The displacement of triglyceride from the particle surface by both saturated and unsaturated MAG could decrease LPL hydrolysis by reducing the available substrate. However, monopalmi-

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tin causes displacement at lower concentration (i.e., equivalent to less hydrolysis) than monolein and thus substrates rich in triglyceride with saturated fatty acids in the 2 position might have slowed hydrolysis. The reduced remnant clearance of 2-monostearin-containing particles may be due to mobility restrictions of surface lipid components, which could alter apolipoprotein structure and interaction on the lipoprotein surface hindering remnant recognition by hepatocytes.

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