

Oil-Binding Capacity of Plastic Fats: Effects of Intermediate Melting Point TAG

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ABSTRACT: The oil-binding capacity (OBC) of fat crystals was investigated as a function of intermediate melting point TAG (IMP-TAG) and stearin composition. Samples were prepared by melting 14% hard fraction (palm–canola stearin and IMP-TAG blends) in 86% liquid oil (olive, canola, safflower, and triolein) and crystallizing the mixture under fast and slow cooling conditions. Under fast cooling conditions, the OBC increased as the IMP-TAG/stearin ratio increased. The OBC is the grams of bound oil (determined by centrifugation) divided by the grams of solid fat (determined by pulse NMR). The maximum OBC was observed at 14% IMP-TAG and 0% stearin. In contrast, under slow cooling conditions, the 14% IMP-TAG and 0% stearin sample did not form crystals, and only free oil was present. The OBC for each liquid oil was lower under slow cooling conditions than under fast cooling conditions when compared at the same IMP-TAG/stearin ratio. Solid fat content and RP-HPLC analyses indicated that IMP-TAG were retained in the crystal structure when processed under fast cooling conditions. RP-HPLC analyses also revealed that TAG with two saturated FA were retained in the crystal structure and that the monosaturated TAG were not. It was concluded that the TAG composition and cooling conditions played an important role in determining the OBC.

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KEY WORDS: Fat crystals, intermediate melting point triacylglycerols, oil-binding capacity, SFC, stearin, supercooling.

The ability of fat crystals to bind and hold a certain amount of liquid oil within their crystal network is dependent on the FA and TAG composition (1,2), thermal properties (3,4), interactions (5,6), and wetting properties (7,8) of the fat crystals. Plastic fats such as shortening and margarine are good examples where the liquid oil is bound and trapped by fat crystals (8–11). This physicochemical property of fat crystals can be called the oil-binding capacity (OBC) and will be defined in this study as: grams of liquid oil bound by one gram of solid fat (based on solid fat content: SFC) measured under specified conditions. Bound oil represents the liquid oil that cannot be separated from fat crystals by centrifugation. Under centrifugal force, the crystal network will collapse and release the trapped oil, which can be collected by decanting, whereas the bound oil remains with the disrupted crystals. The level of liquid oil bound to fat crystals can play an important role in modifying the properties of plastic fats. Understanding the rela-

tionships between OBC of fat crystals, cooling regime, and fat composition may help us to design new fat-based products with desirable properties. The objective of this study was to determine the effects of TAG composition on the OBC of fat crystals by adding varying levels of intermediate melting point TAG (IMP-TAG) and palm–canola stearin to four liquid oils (olive, safflower, canola, and triolein) and crystallizing the mixtures under supercooling (fast and slow) conditions.

EXPERIMENTAL PROCEDURES

Canola oil (refined, bleached, and deodorized) and canola stearin were purchased from Daminco Inc. (Toronto, Canada). Palm stearin was purchased from CanAmera Foods (Toronto, Canada). IMP-TAG (42.2% POP + PPO, 41.0% POS + PSO, and 15.4% SOS + SSO, where P = palmitic, O = oleic, L = linoleic, and S = stearic) were extracted from extra virgin olive oil (12) with yields of 2.4%. Small amounts (1.4%) of POO + PSL and OOS were also detected. The critical pairs listed above indicate possible co-eluting isomers during HPLC analysis. In all subsequent references to IMP-TAG, only the major isomers (POP, POS, SOS) will be listed with the understanding that the co-eluting isomers may be present. Triolein and standard TAG were purchased from Sigma-Aldrich Canada Ltd. (Oakville, Ontario). Extra virgin olive oil and safflower oil were purchased from the supermarket.

Sample preparation. All samples were prepared with 86% liquid oil (olive, safflower, canola oil, and triolein) and 14% solid fat, consisting of palm and canola stearins (40 and 60%, respectively) and/or IMP-TAG. Five levels of stearin and IMP-TAG blends varied concurrently from 0–14% for palm–canola stearin and 14–0% for IMP-TAG. The weight ratios of % stearin/% IMP-TAG were 14:0, 10.5:3.5, 7:7, 3.5:10.5, and 0:14. The mixture of stearin, IMP-TAG, and liquid oils (250 g) was heated to 70°C for 30 min in a 400 mL beaker and mixed vigorously. Approximately 8 g of the completely melted fat (cooled to 50°C) was poured into centrifuge tubes (1.27 × 7.62 cm) and weighed carefully before being subjected to two different cooling programs. Crystallization of each IMP-TAG/stearin blend was replicated three times.

Fast cooling condition. Centrifuge tubes containing samples at 50°C were immediately transferred into an ice-salt bath (–5°C) and held for 5 min to drop the oil/hard fraction blend temperature below its melting point. The samples were then immediately transferred to a freezer and held at –20°C

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for 12 h to complete the crystallization. After 12 h at -20°C , the samples were equilibrated at room temperature (22°C) for 24 h before centrifugation.

Slow cooling condition. Centrifuge tubes containing samples at 50°C were held at room temperature (22°C) for 24 h to slowly cool the oil/hard fraction blend before the samples were centrifuged.

OBC. Both fast- and slow-cooled samples were centrifuged (J2-MC centrifuge; Beckman Instrument Inc., Palo Alto, CA) for 60 min at $25,000 \times g$ and 22°C . The supernatant (free liquid oil) was carefully separated by pouring the oil into a 50-mL beaker and holding the inverted tubes for 5 min to complete separation. The free liquid oil was weighed, and the OBC was calculated with the following equation:

$$\text{oil-binding capacity (OBC)} = \frac{(T - \delta) - \phi}{\delta} \quad [1]$$

where T is the total weight of sample, δ is the amount of solid fat (i.e., IMP-TAG and stearin) determined by pulse NMR (SFC) before centrifugation, and ϕ is the free liquid oil separated after centrifugation. The units for OBC are g bound liquid oil/g solid fat.

SFC. The SFC of the oil/hard fraction blends were measured at 22°C according to AOCS official method Cd 16b-93 (13), using a Bruker pulsed nuclear magnetic resonance (p-NMR) spectrometer, equipped with a Minispec PC/20 data analyzer (Minispec, Milton, Ontario, Canada). NMR tubes were filled with sample at 50°C and treated to fast and slow cooling conditions and equilibrated as previously described. The SFC measurements were replicated three times with four scans per replicate.

GC analysis. The AOCS official method (Ce 2-66) (13), with minor changes, was used to prepare the FAME. The FAME were analyzed using a Shimadzu gas chromatograph (model GC-14 A; Man-Tech Associates Inc., Guelph, Ontario, Canada), equipped with a split-mode injector, FID, and

an SP-2330 (30×0.25 mm i.d., 0.25 mm film thickness) fused-silica capillary column (Supelco, Oakville, Ontario, Canada). The oven was temperature programmed from 145 to 235°C at $6^{\circ}\text{C}/\text{min}$, and the initial and final hold times were 2 and 10 min, respectively. The injector and detector port temperatures were both 260°C , hydrogen gas flow was 30 mL/min, air flow was 300 mL/min, and the carrier gas flow (hydrogen) was 1.0 mL/min. The injection volume was 0.1 μL , and the data were integrated with a Shimadzu Model C-R4A Chromatopac (Man-Tech Associates Inc.). The FA compositions of the oils and stearins were determined (Table 1) with standard FAME purchased from Sigma-Aldrich.

RP-HPLC analysis. The standard AOCS method (Ce 5b-89) (13), with slight modifications, was used to determine the TAG composition of the canola, olive, and safflower oils. The composition of the TAG in the supernatant (free liquid oil after centrifugation) and of the acetone-soluble TAG in the sediment also was determined on the fast- and slow-cooled samples. The separation was performed on two Econosil C18, 5 mm, 4.6×250 mm columns (Alltech, Deerfield, IL) in series. An isocratic system (Waters 600 E; Millipore, Milford, MA) was used. The mobile phase was acetone/acetonitrile (60:40, vol/vol). The sediment was extracted with HPLC-grade acetone (5% sediment in acetone), and 20 μL aliquots were automatically injected (Waters 700 Satellite WISP; Millipore) and eluted at a flow rate of 1 mL/min. The effluent was monitored with a Waters 410 refractive index detector. Column and detector temperatures were at 30°C . The TAG were identified by comparison with standards purchased from Sigma-Aldrich.

RESULTS AND DISCUSSION

All samples prepared under fast cooling conditions and equilibrated at 22°C for 24 h were firm enough to hold their shape. The 14% IMP-TAG samples were softer than the samples with added stearin but not soft enough to flow easily. The samples prepared under slow cooling conditions with 14% IMP-TAG and 0% stearin were completely liquid, whereas samples with 10.5% IMP-TAG and 3.5% stearin, although semisolid at room temperature, were soft enough to flow. Samples with increased amounts of stearin (7, 10.5, and 14%) were firm and did not flow from inverted tubes.

When the oil/hard fraction blends were supercooled and crystallized, most of the liquid oil was physically trapped in the crystal network, and the remainder interacted with the fat crystals through van der Waals forces (10) to form a coating or layer around the fat crystals. Centrifugation of the plastic fat caused the crystal network to collapse and sediment, resulting in the release of the entrapped oil. The released oil was easily drained from the centrifuge tube by decanting, leaving the bound oil in the sediment. Some free oils (0.1%) remained in the centrifuge tube, but their levels were found to be insignificant.

The OBC of the oil/hard fraction blends prepared with olive, canola, and safflower oils [calculated iodine value (IV) = 82, 120, and 149, respectively] (14) and triolein under fast cooling conditions are shown in Table 2. The overall effect of

TABLE 1
FA Composition^a of Oils (canola, olive, and safflower) and Stearin (palm, canola)

| FA | Composition (% area) | | | | |
|------|----------------------|-----------|---------------|--------------|----------------|
| | Canola oil | Olive oil | Safflower oil | Palm stearin | Canola stearin |
| 14:0 | — | — | 0.3 | 1.6 | 0.1 |
| 16:0 | 3.8 | 12.7 | 10.6 | 60.8 | 4.3 |
| 16:1 | 0.2 | 0.8 | 0.2 | — | — |
| 18:0 | 1.9 | 3.0 | 2.2 | 37.5 | 92.4 |
| 18:1 | 60.2 | 77.8 | 13.8 | 0.1 | 0.7 |
| 18:2 | 20.7 | 4.5 | 72.2 | — | — |
| 18:3 | 9.8 | 0.7 | 0.2 | — | — |
| 20:0 | 0.6 | 0.3 | 0.2 | — | 1.6 |
| 20:1 | 1.7 | 0.2 | 0.1 | — | — |
| 22:0 | 0.3 | — | 0.1 | — | 0.6 |
| 22:1 | 0.3 | — | — | — | — |
| 24:0 | 0.2 | — | — | — | 0.3 |
| 24:1 | 0.3 | — | — | — | — |
| S/U | 0.07 | 0.19 | 0.15 | — | — |

^aS/U, ratio of total saturated FA/total unsaturated FA. —, undetected.

TABLE 2
Oil-Binding Capacity^a (OBC) and Solid Fat Content (SFC) of Liquid Oil/Hard Fraction Blends Crystallized Under Fast Cooling Condition

| Palm– canola stearin (%) | IMP- TAG ^b (%) | Olive oil | | Safflower oil | | Canola oil | | Triolein | |
|--------------------------------|---------------------------------|--------------|------------|---------------|------------|--------------|------------|--------------|------------|
| | | OBC (g/g) | SFC (%) | OBC (g/g) | SFC (%) | OBC (g/g) | SFC (%) | OBC (g/g) | SFC (%) |
| 14 | 0 | 6.2 ± 0.1 | 11.7 ± 0.1 | 6.3 ± 0.2 | 11.1 ± 0.2 | 6.7 ± 0.3 | 11.1 ± 0.1 | 7.8 ± 0.1 | 9.4 ± 0.1 |
| 10.5 | 3.5 | 7.3 ± 0.1 | 10.5 ± 0.1 | 7.4 ± 0.1 | 9.7 ± 0.2 | 7.8 ± 0.2 | 10.1 ± 0.1 | 7.8 ± 0.2 | 10.1 ± 0.1 |
| 7 | 7 | 9.5 ± 0.2 | 8.3 ± 0.2 | 8.9 ± 0.1 | 7.8 ± 0.15 | 10.0 ± 0.2 | 8.2 ± 0.2 | 8.7 ± 0.1 | 6.5 ± 0.1 |
| 3.5 | 10.5 | 13.3 ± 0.1 | 5.2 ± 0.1 | 13.8 ± 0.5 | 5.1 ± 0.1 | 13.0 ± 0.2 | 5.3 ± 0.1 | 11.5 ± 0.1 | 4.1 ± 0.1 |
| 0 | 14 | 29.3 ± 3.0 | 1.5 ± 0.1 | 26.7 ± 2.2 | 1.3 ± 0.1 | 20.8 ± 0.2 | 1.4 ± 0.1 | 27.3 ± 0.2 | 1.1 ± 0.2 |

^aOBC was measured at 22°C after centrifugation. Units are g bound liquid oil per g solid fat.

^bIMP-TAG, intermediate melting point-TAG.

the stearin/IMP-TAG ratio was significant on the OBC ($P < 0.001$) for all blends treated under fast cooling conditions.

Although the samples with 14% IMP-TAG in olive, canola, and safflower oils and triolein had SFC values of only 1.5, 1.4, 1.3, and 1%, respectively, the OBC were higher than those samples with added stearin (Table 2). The lowest OBC values were observed when the stearin was 14% and the IMP-TAG was 0%. In the samples with 14% IMP-TAG, approximately 90% of the IMP-TAG dissolved in the liquid oil leaving only 1 to 1.5% solids that formed a nonflowing opaque mass that retained a significant amount of liquid oil after centrifugation (Table 2). These results show that a small amount of IMP-TAG crystals can hold a large amount of liquid oil, possibly through interactions between fat crystals, dissolved IMP-TAG, and liquid oil. The 14% IMP-TAG samples formed an opaque mass with a consistency similar to a weak gel. After centrifugation, the sediment filled approximately one-half of the tube and weighed substantially more than the total weight of added IMP-TAG. It was hypothesized that the dissolved IMP-TAG played an important role in forming the opaque structure under fast cooling conditions. When the crystals develop under fast cooling conditions, the dissolved IMP-TAG may act as a bridge between fat crystals and liquid oil. The wetting of crystals by liquid oils should be enhanced if the FA composition, TAG composition, and overall polarity between liquid oil and crystals are similar. TAG with short-chain FA and/or long-chain unsaturated FA have lower equivalent carbon numbers (ECN) (15) and greater polarity than the saturated stearin TAG (16,17). Accordingly, the dissolved IMP-TAG and the TAG from the liquid oils (Table 3), which have comparable ECN, should more easily wet the IMP-TAG crystals. Because of their lower polarity and higher ECN (TAG were shown to be composed mainly of S and P, Table 1) the stearin crystals should interact less with the liquid oil. This can be seen with the 14% IMP-TAG samples, where the surface of the fat crystals contains only IMP-TAG and the resulting values for OBC are the highest of all the samples tested (Table 2). When the stearin level in the hard fraction blend was increased to 3.5:10.5 (stearin/IMP-TAG), the composition of the crystals formed under fast cooling conditions would be mostly stearin with possibly some IMP-TAG incorporation. The appearance of the nonliquid material changed from an opaque mass to a white solid.

Because of the higher amounts of stearin crystals on the surface, the amount of wetting and interaction with dissolved IMP-TAG and liquid oil (on a per gram solid basis) decreased. This resulted in a lower OBC when compared to the 14% IMP-TAG samples. As the amount of IMP-TAG was decreased further and the stearin increased, the OBC decreased again for the same postulated reasons. In samples with only stearin (14%), the wetting and interaction of the crystals with liquid oil was the lowest due to the low polarity of stearin crystals. Based on these findings, a schematic of the possible interactions is as follows:

TABLE 3
TAG Composition of Canola, Olive, and Safflower Oils

| | TAG | Canola oil (%) | Olive oil (%) | Safflower oil (%) | ECN ^a |
|----|----------------------|-------------------|------------------|----------------------|------------------|
| 1 | Unknown ^b | 2.3 | 3.0 | 4.7 | — |
| 2 | LnLnLn | — | — | — | 36 |
| 3 | LnLnL | 0.2 | — | — | 38 |
| 4 | LnLL | 0.1 | 0.3 | — | 40 |
| 5 | LnLnO | 0.5 | 0.5 | 0.9 | 40 |
| 6 | LLL | 2.7 | — | 38.1 | 42 |
| 5 | LnLO | 6.9 | 0.6 | 0.2 | 42 |
| 6 | LnLP | 0.1 | — | — | 42 |
| 7 | LLO | 5.5 | 0.9 | 18.7 | 44 |
| 8 | LnOO | 12.8 | 2.9 | — | 44 |
| 9 | LLP | 2.0 | 0.6 | 16.3 | 44 |
| 10 | LOO | 20.8 | 6.7 | 4.2 | 46 |
| 11 | LOP | 4.7 | 5.4 | 4.6 | 46 |
| 12 | PLP | — | 1.1 | 5.0 | 46 |
| 11 | OOO | 30.0 | 44.7 | 0.4 | 48 |
| 13 | POO | 4.6 | 24.6 | 4.5 | 48 |
| 14 | SLP | — | — | — | 48 |
| 13 | POP | 0.3 | 2.9 | — | 48 |
| 14 | PPP | 1.5 | 0.1 | 0.9 | 48 |
| 15 | SOO | 3.4 | 4.3 | 1.0 | 50 |
| 16 | SLS | 0.1 | 0.3 | 0.3 | 50 |
| 17 | SOP | 0.3 | 0.6 | — | 50 |
| 18 | PPS | 0.9 | — | — | 50 |
| 19 | SOS | 0.3 | 0.5 | — | 52 |
| 20 | PSS | — | — | 0.2 | 52 |
| 21 | SSS | — | — | — | 54 |

^aECN, equivalent carbon number calculated using equation in Reference 15; Ln, linolenic acid; L, linoleic acid; O, oleic acid; P, palmitic acid; S, stearic acid; —, undetected.

^bMono-, di-, and triglycerides.

TABLE 4
OBC^a and SFC of Liquid Oil/Hard Fraction Blend Crystallized Under Slow Cooling Condition

| Palm–canola stearin (%) | IMP-TAG ^b (%) | Olive oil | | Safflower oil | | Canola oil | | Triolein | |
|-------------------------|--------------------------|-----------------|------------|---------------|------------|------------|------------|-----------|-----------|
| | | OBC (g/g) | SFC (%) | OBC (g/g) | SFC (%) | OBC (g/g) | SFC (%) | OBC (g/g) | SFC (%) |
| 14 | 0 | 5.0 ± 0.1 | 11.8 ± 0.1 | 5.2 ± 0.1 | 11.2 ± 0.1 | 5.5 ± 0.1 | 11.1 ± 0.1 | 6.5 ± 0.3 | 9.5 ± 0.3 |
| 10.5 | 3.5 | 5.7 ± 0.2 | 9.5 ± 0.1 | 5.5 ± 0.1 | 9.5 ± 0.1 | 5.6 ± 0.1 | 9.3 ± 0.1 | 7.1 ± 0.1 | 8.2 ± 0.1 |
| 7 | 7 | 4.9 ± 0.2 | 6.9 ± 0.1 | 5.6 ± 0.1 | 7.0 ± 0.2 | 5.4 ± 0.1 | 6.6 ± 0.1 | 8.1 ± 0.1 | 5.3 ± 0.1 |
| 3.5 | 10.5 | 5.5 ± 0.1 | 4.2 ± 0.1 | 8.0 ± 0.1 | 3.9 ± 0.1 | 7.1 ± 0.0 | 3.8 ± 0.1 | 8.3 ± 0.2 | 3.3 ± 0.1 |
| 0 | 14 | UD ^b | 0.00 | UD | 0.00 | UD | 0.00 | UD | 0.00 |

^aOBC was measured at 22°C after centrifugation.

^bUD, undefined (samples with 0% SFC). For other abbreviations see Table 2.

fat crystals ... IMP-TAG ... liquid oil

Under slow cooling conditions, the effect of the stearin/IMP-TAG ratio was also significantly ($P < 0.01$) related to OBC. Under slow cooling conditions, all IMP-TAG (14% level) dissolved in the liquid oil and the sample registered zero solids by p-NMR (Table 4). Because no crystals formed, all the liquid oil was free. In samples with 3.5% stearin and 10.5% IMP-TAG, the stearin fraction crystallized and only a small amount of crystalline IMP-TAG appeared to be present. The main factor affecting the OBC of these samples appeared to be the wetting and interaction of stearin crystals with dissolved IMP-TAG and liquid oil. Under these conditions, the overall OBC was lower than the fast-cooled samples.

Normally the OBC of plastic fats would decrease as the total amount of fat crystal decreases. However, under slow cooling conditions, decreasing levels of stearin crystals did not decrease the OBC (Table 4). The OBC remained constant or appeared to increase slightly as stearin dropped to 3.5%. The reason for this effect may be related to the wetting properties of the dissolved IMP-TAG. As the amount of stearin decreased, it was compensated for by increasing levels of dissolved IMP-TAG, which facilitated crystal wetting.

When used at 14%, stearin under both fast and slow cooling conditions was partly dissolved in the liquid oil and had lower SFC than the amounts actually added (Table 2 and 4). However, as the IMP-TAG levels increased above 3.5% under fast cooling conditions, the SFC increased above the added stearin levels. This increase in solids could only come from the added IMP-TAG, indicating some of the IMP-TAG crystallized and was retained in the stearin crystals. The properties of the stearin crystals would be altered by the IMP-TAG incorporation and might increase their interaction with dissolved IMP-TAG and liquid oil. The incorporation of IMP-TAG was not observed under slow cooling conditions. Generally, under slow cooling conditions the SFC was either below or very close to the added stearin levels (Table 4). This would be expected if all the IMP-TAG dissolved in the liquid oil along with a small amount of the stearin.

Structural role of IMP-TAG on OBC. Under fast cooling conditions, the high-melting and IMP-TAG will crystallize at about the same time. Therefore, the crystallization order (from high- to low-melting point TAG) will not be followed, as it

would be under slow cooling conditions. This provides an opportunity for IMP-TAG to crystallize along with stearin TAG and become incorporated into the stearin crystals.

The proposed incorporation of IMP-TAG into the stearin crystal is based on the SFC results discussed above and the following evidence. After cooling and centrifuging the olive oil and 14% IMP-TAG mixture, the TAG compositions of the supernatant (free liquid oil) and the sediment were determined by RP-HPLC (Table 5, part A). Because no crystals were formed under slow cooling conditions, the TAG composition of the supernatant was the sum of olive oil and dissolved IMP-TAG. When a small amount of crystal formed (1.5%) under fast cooling conditions, the sediment was composed of crystallized IMP-TAG (POP, POS, SOS) and bound liquid oil (olive oil + dissolved IMP-TAG). The analysis of

TABLE 5
Composition of POP, POS, and SOS in the Supernatant and Sediment (crystal) of Liquid Oil/Hard Fraction Blends (olive oil/palm–canola stearin, IMP-TAG) After Crystallization Under Fast and Slow Cooling Conditions

| TAG profile | Relative composition of POP, POS, and SOS | | | |
|---|---|-----------------|--------------------|----------------------|
| | Fast cooling | | Slow cooling | |
| | Supernatant (%TAG) | Sediment (%TAG) | Supernatant (%TAG) | Sediment (%TAG) |
| A: Olive oil (86%): palm–canola stearin (0%): IMP-TAG (14%) | | | | |
| POP + PPO | 4.2 | 4.3 | 4.5 | No sed. ^a |
| POS + PSO | 4.9 | 6.2 | 5.8 | No sed. |
| SOS + SSO | 1.7 | 5.0 | 3.4 | No sed. |
| OOS | 5.3 | 4.0 | 5.2 | No sed. |
| B: Olive oil (86%): palm–canola stearin (10.5%): IMP-TAG (3.5%) | | | | |
| POP + PPO | 2.5 | 2.7 | 3.3 | 2.7 |
| POS + PSO | 1.1 | 2.3 | 2.5 | 2.3 |
| SOS + SSO | 0.5 | 1.1 | 1.0 | 0.9 |
| OOS | 5.2 | 5.4 | 5.7 | 5.3 |
| C: Olive oil (86%): palm–canola stearin (3.5%): IMP-TAG (10.5%) | | | | |
| POP + PPO | 3.3 | 5.1 | 3.4 | 3.6 |
| POS + PSO | 3.8 | 5.4 | 4.6 | 3.9 |
| SOS + SSO | 1.3 | 2.8 | 2.3 | 1.8 |
| OOS | 5.2 | 5.3 | 5.2 | 4.3 |

^aUnder slow cooling conditions, the IMP-TAG dissolved in liquid oil. For abbreviations see Tables 2 and 3.

sediment should therefore reflect the composition of the olive oil, dissolved IMP-TAG, and the crystallized IMP-TAG, whereas the composition of the supernatant should reflect the composition of the olive oil plus dissolved IMP-TAG minus the small amount of IMP-TAG that crystallized. The results showed that the greatest change in TAG profile was with SOS, which decreased to 1.7% in the supernatant and increased to 5% in the sediment (Table 5, part A). A small change was seen with POS, and very little change with POP. These results indicate that SOS was the predominant TAG that crystallized (in the absence of stearin) under fast cooling conditions followed by POS and POP. Among the IMP-TAG, SOS has the highest m.p. (9) and should form the greatest amount of crystal. Similar results were obtained with the other oils (safflower, canola, and triolein), but the changes in TAG composition were not as dramatic.

In the presence of 10.5% stearin and 3.5% IMP-TAG, the amount of IMP-TAG in the sediment under fast cooling conditions was higher than the corresponding supernatant, indicating that some IMP-TAG were crystallized and retained in the stearin crystal (Table 5, part B). This amount cannot be seen in Table 2, since some stearin dissolved in liquid oil and the SFC value (10.5%) can represent both stearin and IMP-TAG. Because acetone dissolves the IMP-TAG and liquid oil but not stearin (the solubility of canola stearin in acetone is only 0.46% at room temperature), the RP-HPLC results represent the TAG from the IMP-TAG and olive oil. Although there was crystal formation under slow cooling conditions, these crystals were from the stearin fraction only. The IMP-TAG did not crystallize with the stearin fraction under slow cooling conditions, as shown in Table 5, part B. The amounts of POP, POS, and SOS in the sediment were nearly equal or slightly less than in the supernatant. The measured POP, POS, and SOS in sediment were due to bound liquid oil (olive oil + dissolved IMP-TAG). The amounts of IMP-TAG in the 3.5% stearin and 10.5% IMP-TAG blends were also higher in the sediment than in the supernatant when crystallized under fast cooling conditions (Table 5, part C). There appears to be a direct relationship between the amount of IMP-TAG (dissolved and crystalline) and the increase in OBC under fast cooling conditions. For the olive oil sample, the OBC increased from 6.2 to 29.3 g/g as the IMP-TAG concentration increased from 0 to 14%, respectively (Table 2).

It should be noted that OOS, which contains only one saturated FA, did not behave the same as POS and SOS (Table 4). All chromatograms showed only small changes in the percentage in both supernatant and sediment, indicating little incorporation into the crystal structure. The presence of OOS in the sediment was due only to bound olive oil. Similar results were obtained with POO (data not shown). We hypothesized that TAG with one saturated acid cannot be crystallized or incorporated into the crystal structure under the given conditions, whereas IMP-TAG with two saturated acids (POS and SOS) were incorporated into the crystal structure.

In general, simply by increasing the SFC with stearin or IMP-TAG crystals, the absolute amount of bound oil can be

increased because of a larger crystal surface area. However, the type of TAG, wetting property, liquid oil/crystal interaction, and cooling program are additional factors that should be considered when attempting to improve OBC.

Centrifugation and low resolution p-NMR can be used to measure the OBC of oil/hard fraction blends. The type of IMP-TAG and cooling conditions are important factors in determining the OBC. It is proposed that the IMP-TAG are able to increase the OBC due to their intermediate polarity, allowing them to act as bridges between high-melting TAG and liquid oil and that the incorporation of IMP-TAG into the crystal structure improved the wetting ability of crystals and hence the OBC. Among the IMP-TAG, disaturates are more likely to be incorporated into the crystal structure than monosaturated TAG.

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