SUPPLEMENTARY MATERIAL

Sample preparation

Distilled monoacylglycerols (MAGs) were kindly provided by Danisco (Kansas, MO), and included Dimodan® HS K-A (10% monopalmitin, 90% monostearin), with fatty acids predominantly at positions sn-1 and sn-3. Sodium hydroxide (2N NaOH) was obtained from Fischer (St. Louis, MO), canola oil (low-erucic rapeseed oil) was purchased in a local supermarket. Deionized water was used in all experiments and was of milliQ grade.

A typical 10% (w/w) stock of HS K-A in vegetable oil - all oils performed equally well - was prepared by melting 10g of the solid MAG HS K-A (m.p. ~73°C) and 500mg of sodium stearoyl lactylate (SSL) or stearic acid powders in 89.5g of oil at 70°C for 30 minutes. Appropriate volume fractions of 70°C 0.2N NaOH, were then added to the MAG-oil stock in a glass bowl heated to 70°C. The material was mixed with the aid of an electric hand mixer until a macroscopically homogeneous white paste was obtained, and then allowed to set undisturbed at room temperature (22°C). The material set almost immediately. For 100mL batches, setting was complete within 30 minutes. The mixture had to contain at least 4% (w/w) distilled monoglyceride for proper gel formation and stability. Added salts and proteins generally decreased stability and/or prevented gel formation.

Sample characterization

Powder X-ray diffraction (XRD) measurements were conducted using an in-house diffractometer with Cu source (λ=1.54 Å) and Position Sensitive Detectors. Very small
angle XRD measurements were carried out at the Austrian Small Angle X-ray Scattering (SAXS) beamline (http://www.ibr.oeaw.ac.at/beamline) at Elettra (Sincrotrone Trieste, Italy). Confocal laser scanning microscopy was performed using a Leica TCS SP II confocal laser scanning microscope. For confocal microscopy, samples were stained with Coumarin which is soluble in the aqueous phase and Nile Red for the oil phase. Polarized light microscopy was carried out using a Leica DM RXA2 upright light microscope (Leica Microsystems, Toronto, Canada) equipped with a digital monochrome camera (Q Imaging Retiga® 1300, Vancouver, Canada). Dynamic shear loss ($G''$) and storage ($G'$) were obtained using a TA Instruments AR2000 rheometer at 20°C by stress sweeps using a temperature controlled parallel plate geometry at a frequency of 1Hz.

**Acute human ingestion trials**

Five male and four female subjects were recruited for this study. Approval for the study was received from the Research Ethics Committee of the University of Waterloo and each participant provided written informed consent prior to participation. Questionnaires were used to determine medical history and exercise habits for each participant. Height and weight measurements were obtained and body mass index (BMI) calculated. The average BMI of the subjects was $25.2 \pm 2.8 \text{ kg/m}^2$, while the average age was $24 \pm 2$ years (mean ± standard deviation).

The subjects completed two separate trials in which they consumed one of the two test meals in randomized order. The test meals consisted of two pieces of 100% whole wheat toast with either a canola oil-water mixture (CO) or a structured oil-water mixture (MAG...
Gel). The subjects consumed 80g of the MAG Gel (4.8g monostearin, 43.2g of canola oil, 32g water), or 80g of the CO-water mixture (48g CO, 32g water), but no monoglycerides. The CO was mixed with water in proportions equivalent to those of the MAG Gel. The test meal was ingested within ten minutes. Each trial was six hours in duration during which the subjects were permitted to drink only one liter of water. Subjects were instructed to refrain from alcohol and strenuous exercise for 24 hours prior to each trial. They were also not permitted to consume any food or caffeine after 9pm the night before. The trials were separated by seven days and conducted in a random order.

Blood samples were obtained throughout each trial using a forearm venous catheter. A baseline sample was taken prior to administration of the test meal and at 30, 60, 90, 120, 150, 180, 240, 300 and 360 minutes after meal consumption. Serum was separated from untreated whole blood by centrifugation (21°C, 10 minutes, 1800g), while heparin and EDTA plasma was obtained by centrifugation (4°C, 10 minutes, 1100g) after adding either 15µL of heparin (5U/µL) or 60µL of EDTA (0.05mg/µL) respectively to 1.5 ml of whole blood. All serum and plasma samples were stored at -70°C until analysis.

Serum triglyceride (TG), cholesterol (CHOL) and high-density lipoprotein (HDL) levels were determined at a third party, accredited diagnostic laboratory (Toronto Medical Laboratories; Toronto, Ontario, Canada) by automated methods employing a Bayer Advia 1650 auto analyzer. The Friedewald equation was used to calculate the low-density lipoprotein (LDL) levels. The serum TG responses over time are expressed as the difference from baseline, which was established using t=0 and t=30 measures. Free fatty
acids (FFA) were measured in quadruplicate from EDTA plasma by using the NEFA
ACS-ACOD method with a kit provided by Wako Chemicals GmbH (Neuss, Germany).
The plasma FFA responses over time are expressed as the difference from baseline,
which was measured at 0 hours. Glucose concentration was determined from heparinized
plasma samples in triplicate using a spectrophotometric enzymatic assay. The assay was
based on the coupled glucose oxidase/peroxidase enzymatic reactions and all reagents
were obtained from Sigma (St. Louis, Missouri, USA). Insulin was determined in
duplicates from heparinized plasma using a Coat-A-Count Radioimmunoassay Kit
(Diagnostic Product Corporation: Los Angeles, California, USA).

The trapezoidal method was used to calculate the specified net AUC for each of the
variables (3-6h: TG; 0-6h: FFA, glucose, insulin). Differences between the two trials
were assessed for significance using a paired t-test (p<0.05). Analyses were completed
using GraphPad Prism Version 4.03 for Windows, GraphPad Software: San Diego,
California, USA.