Supporting information for:

Biobased Fat Mimicking Molecular Structuring Agents for Medium Chain Triglyceride and other Edible Oils

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Spectroscopic Characterization for RKG8, RKG18, and RKGO

Data for (**RKG8**): Raspberry Ketone Glucoside Caprylate (((2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(4-(3-oxobutyl)phenoxy)tetrahydro-2H-pyran-2-yl) methyl octanoate): FT-IR (neat) 3489 (m, νO-H), 3207 (b, νO-H), 2920 (m, sp^3 νC-H_2), 2850 (m, sp^3 νC-H_2), 1736 (s, ester νC=O), 1738 (s, ester νC=O), 1711 (s, ketone νC=O), 1512 (s, sp^2 Ar δC=C), 1230 (s, ester νC-O), 1009 (s, ether νC-O) cm-1. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC): δ 7.07 (d, 2H) 6.94 (d, 2H), 4.83 (d, 1H), 4.45 (d, 1H) 4.31 (d, 1H), 3.65 (s, 2H), 3.57 (s, 1H), 3.46 (s, 1H) 2.78 (d, 4H), 2.35 (t, 2H), 2.12 (s, 3H) 1.60 (t, 2H), 1.26 (s, 8H), 0.86 (s, 3H). ^{13}C ($CDCl_3$, 300 MHz, 25 ºC) 208.23 (ketone C=O), 173.38 (ester C=O), 156.21 (aryl), 135.20 (aryl), 130.68 (aryl), 128.60 (aryl), 117.83 (2C, aryl) 77.97 (gluc-C), 76.09 (gluc-C), 74.74 (gluc-C), 71.62 (gluc-C), 69.77 (gluc-C), 66.07 (gluc-CH_2), 45.08 (ketone α-CH_2), 36.04, 31.84, 29.08 (2C), 27.81, 25.14, 24.37, 22.74, 13.89 (fatty acid CH_3). MS (ESI) m/z (MH^+) 453.24, M.P.R. 96 - 97°C. Elem. Anal. Pred. C: 63.70, H: 8.02, Calc. C: 63.53, H: 8.02

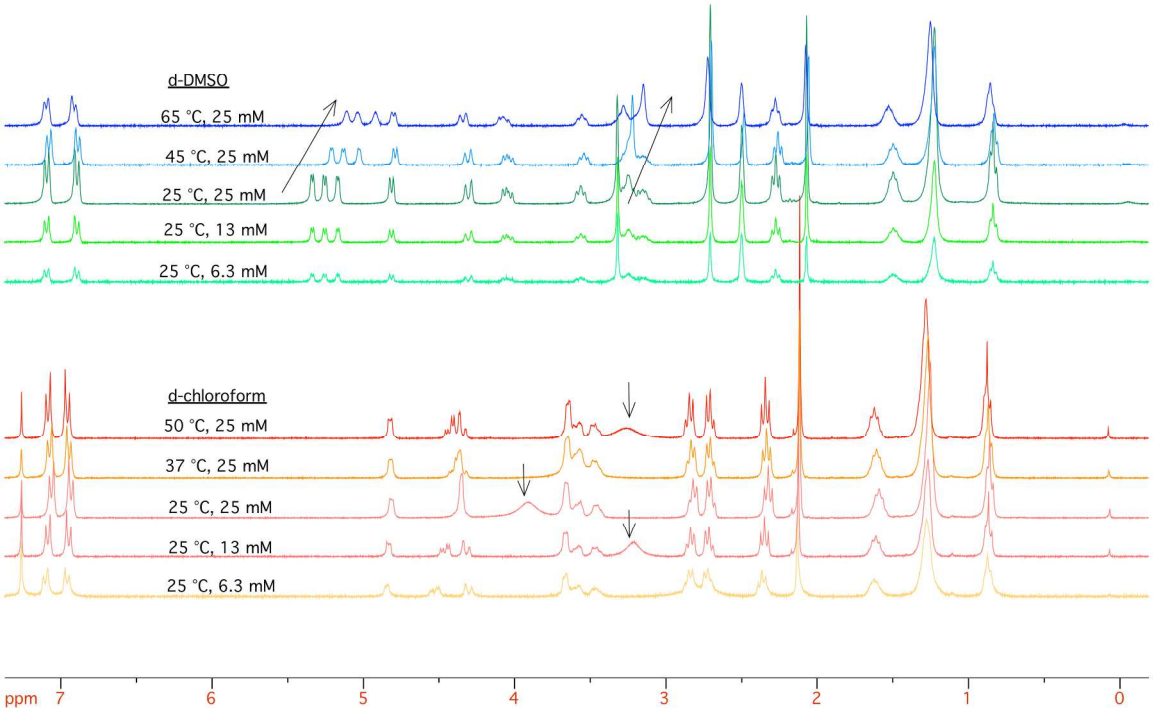
PARAGRAPH BELOW - JUSTIFICATION NEEDED

Data for (**RKG18**): Raspberry Ketone Glucoside Stearate (((2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(4-(3-oxobutyl)phenoxy)tetrahydro-2H-pyran-2-yl) methyl stearate): FT-IR (neat) 3489 (m, νO-H), 3207 (b, νO-H), 2918 (m, sp^3 νC-H_2), 2850 (m, sp^3 νC-H_2), 1736 (s, ester νC=O), 1711 (s, ketone νC=O), 1512 (s, sp^2 Ar δC=C), 1230 (s, ester νC-O), 1009 (s, ether νC-O) cm-1. ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.06 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 4.80 (m, 1H), 4.33 (d, J = 11.6 Hz, 1H), 3.64-3.46 (m, 4H), 3.21 (d, J = 1.1 Hz, 3H), 2.81-2.70 (t, 4H), 2.31 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 1.67 (t, J = 6.5 Hz, 2H), 1.27 (s, 28H), 0.86 (d, J = 6.7 Hz, 3H). ^{13}C ($CDCl_3$, 300 MHz, 25ºC) 209.3 (ketone C=O), 175.8 (ester C=O), 157.1 (aryl), 136.0 (aryl), 131.8 (aryl), 129.6 (aryl), 118.8 (2C, aryl) 78.9 (gluc-C), 76.1 (gluc-C), 74.7 (gluc-C), 71.2 (gluc-C), 70.7 (gluc-C), 66.1 (gluc-CH_2), 46.8 (ketone α-CH_2), 37.4, 31.8, 29.8 (2C), 27.8, 25.4, 24.2, 22.4, 14.9 (fatty acid CH_3). MS (ESI) m/z (MH^+) 593.42, M.P.R. 111 – 113 °C. Yields for reaction with methyl stearate: 62%, with vinyl stearate: 87%

JUSTIFICATION NEEDED

Data for (**RKGO**): Raspberry Ketone Glucoside Oleate (((2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(4-(3-oxobutyl)phenoxy)tetrahydro-2H-pyran-2-yl) methyl oleate): FT-IR (neat) 3493 (m, νO-H), 3260 (b, νO-H), 2923 (m, sp^3 νC-H_2), 2853 (m, sp^3 νC-H_2), 1740 (s, ester νC=O), 1709 (s, ketone νC=O), 1513 (s, sp^2 Ar δC=C), 1231 (s, ester νC-O), 1069 (s, ether νC-O) cm-1. ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.15-7.03 (m, 2H), 7.00-6.90 (m, 2H), 5.41-5.26 (m, 1H), 4.94-4.74 (m, 1H), 4.59-4.46 (m, 1H), 4.38-4.20 (m, 1H), 3.80-3.34 (m, 5H), 3.30-3.05 (m, 2H), 3.04-2.48 (m, 7H), 2.45-2.23 (m, 2H), 2.23-2.03 (m, 3H), 1.73-0.44 (m, 31H). ^{13}C ($CDCl_3$, 300 MHz, 25ºC) 207.9 (ketone C=O), 173.4 (ester C=O), 156.7 (aryl) 135.4 (aryl) 130.8 (aryl) 128.5 (C=C) 117.8 (aryl) 115.9 102.0 100.1 76.9 (gluc-C) 74.5 (gluc-C) 73.7 (gluc-C) 69.9 57.7 46.7 45.2 29.5 (fatty acid CH_2) 14.0 (fatty acid CH_3) MS (ESI) m/z (591.38) M.P.R. 96-98 °C. Yield for reaction with vinyl oleate: 56%

SI Figure 1. ^{1}H NMR Spectra for RKG8 in polar/non-polar solvents



NMR Spectra of R8 Solutions demonstrating inter- and intra-molecular hydrogen bonding. Arrows indicate shifting peaks indicative of changes in hydrogen bonding.

SI Table 1. Gelation Index and Minimum Gelation Concentration Values

Solvent	Rasp Ketone Glucoside	RKG8	RKG18	RKGO
Edible Oils				
Hazelnut Oil	I	G (0.26)	G (0.24)	G (0.56)
Coconut Oil	I	G (0.27)	G (0.28)	G (0.54)
Grape seed Oil	I	G (0.25)	G (0.30)	G (0.66)
Red Palm Oil	I	G (0.34)	G (0.36)	G (0.72)
Jojoba Oil	I	G (0.25)	G (0.26)	G (0.48)
Organic Solvents				
Hexanes	I	G (2.1)	G (0.24)	I
Mineral Oil	I	G (1.4)	G (0.24)	G (0.80)
Toluene	PS	G (0.5)	G (0.36)	G (0.73)
Water	PS	I	I	I

Gelation, solubility and concentration data for RKG8, RKG18, and RKGO gels. Raspberry ketone derivatives formed gels (G, MGC wt. % mg/mL) in edible and inorganic oils, were soluble (S) or partially soluble (PS) in polar aprotic solvents (ethyl acetate, acetone, DMSO, methanol and ethanol), and insoluble (I) in water. The low MGCs in edible oils indicate a consistent gel irrespective of oil composition.

SI Table 2. Temperature of Gelation values for gelators and gels

Sample (Neat)	Melting Point (°C)
RKG	113-115
RKG8	96-97
RKG18	111-113
RKGO	96-98
Sample (Gel)	T_{gel} (°C)
5 wt. % RKG8 in Toluene	48-50
5 wt. % RKG8 in Olive Oil	108-110
5 wt. % RKG8 in Coconut Oil	106-107
5 wt. % RKG18 in Coconut Oil	111-112
5 wt. % RKGO in Coconut Oil	105-109

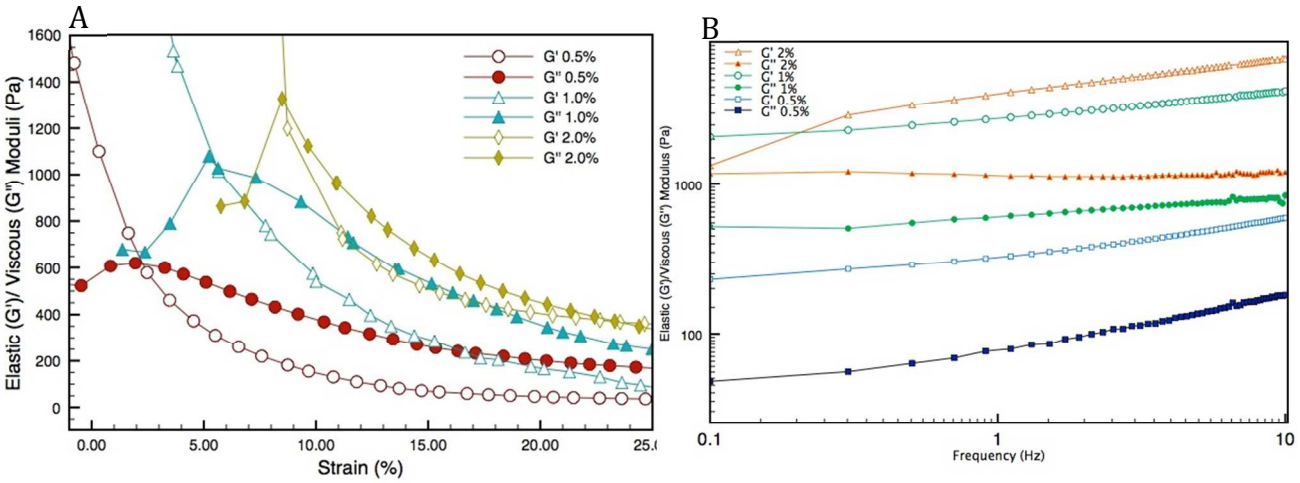
Melt temperatures of neat gelators and gels for comparison.

SI Table 3. XRD Peak values for Gelator Polymorphs

XRD	Small Angle		Wide Angle
Gelator	**Angle (2θ)**	**Distance (Å)**	**Peaks (Å)**
RKG8 Crystal	3.30	26.7	7.41, 5.90, 5.11, 4.23, 3.71, 3.53, 2.96
RKG8 Bulk	2.99	29.6	7.10, 5.94, 5.16, 4.39, 3.74, 3.64, 3.54, 2.96
RKG8 Fibres	2.99	29.6	7.08, 5.93, 4.24, 3.83, 3.73
RKG18 Fibres	2.17	40.8	8.38, 7.65, 6.67, 6.52, 3.82, 3.60, 3.47

Diffraction peaks for RKG8 polymorphs and RKG18 samples. β' peaks are highlighted.

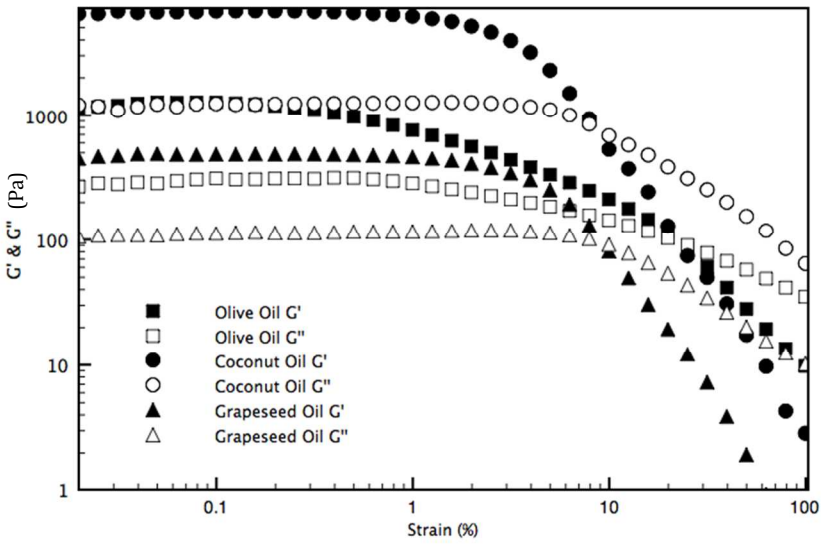
SI Figure 2. Dynamic Oscillatory Rheology of Coconut Oil Gels



Oscillatory rheometry studies of coconut oleogels. A) Strain sweep curve of various coconut oleogel concentrations to highlight the effect of concentration of gel strength. B) Frequency sweep in the linear viscoelastic region of the same oleogels indicating the gelatinous nature of the binary mixtures

Rheological Characterization of Gels: Methods. Oscillatory rheological measurements were performed on a stress-controlled rheometer (AR 2000 ex) with a cone and plate geometry (1° 58′ 47″ angle and 40 mm diameter with a truncation gap of 45 μm). 1 mL of gel was loaded onto the plate, and the cone was lowered to minimize the truncation gap. Precautions were taken to minimize shear-induced disruption of the gel network: before experiments samples were equilibrated within the geometry for 10 minutes. Excess gel was trimmed away from the cone to ensure optimal filling. Yield strain (σ_y) was examined for coconut oil gels (0.5, 1.0 and 2.0% caprylate gels in coconut oil) by performing oscillatory strain sweep measurements from 0.01 to 100% deformation at a fixed frequency of 1 Hz. Oscillatory frequency sweep measurements were performed in the frequency domain of 0.01 - 10 Hz, with a constant strain of 0.1%, which is within the determined linear viscoelastic regime of the samples. Experiments were run at 30 °C, above the melting point of coconut oil, and repeated twice for each concentration.

SI Figure 3. Comparison of Oil Type on Gel Strength and Yield Strain



The strength of the gels increases with a decrease in the percent of unsaturations in the triglycerides (saturated fat content: coconut > olive > grapeseed oil).