

Synthesis and Physical Properties of Symmetrical and Non-symmetrical Triacylglycerols Containing Two Palmitic Fatty Acids

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Abstract A series of symmetrical (ABA) and non-symmetrical (AAB) triacylglycerol (TAG) isomers containing “A,” palmitic (P; 16:0) acid, and “B,” either oleic (O; 9c-18:1), elaidic (E; 9t-18:1), linoleic (L; 9c,12c-18:2) or linolenic (Ln; 9c,12c,15c-18:3) fatty acids were synthesized by esterification of the thermodynamically more-stable 1,3-di- or 1(3)-monoacylglycerols [1,3-DAG or 1(3)-MAG], respectively. 1,3-dipalmitoylglycerol (1,3P-DAG) was esterified with O, L or Ln acid to prepare the symmetrical TAG isomers POP, PLP and PLnP, while the O- E-, L- and Ln-1(3)MAG precursors, synthesized or obtained commercially, were esterified with P acid to prepare the non-symmetrical TAG isomers OPP, EPP, LPP and LnPP, respectively. The drop point(s), solid fat content and melting point values of the synthesized TAG were determined. The 1,3-dipalmitoylglycerol (1,3P-DAG) and 1(3)P-MAG precursors were prepared, in multi-gram quantities, by partial glycerolysis (glycerol/*p*-toluenesulfonic acid) of tripalmitin. After fractionation by silica gel chromatography, the 1(3)P-MAG and 1,3P-DAG isomers (ca. 80% of total MAG or DAG) were purified (>98%) by crystallization from acetone [silver ion-HPLC was utilized to determine the structural purities of the DAG (or MAG) precursors, and the synthesized TAG]. Esterification of the

appropriate, thermodynamically more-stable MAG or DAG precursors was found to be a very versatile method for synthesis (in 80–90% yields) of multi-gram (3–5 g) quantities of symmetrical and non-symmetrical TAG isomers, in chemical and structural purities of >96 and 97–99%, respectively.

Keywords Triacylglycerols · *cis* · *trans* · Synthesis · Palmitic · Oleic · Elaidic · Linoleic · Linolenic · NMR · SFC

Abbreviations

TAG	Triacylglycerol
DAG	Diacylglycerol
MAG	Monoacylglycerol
P	Palmitic 16:0
O	Oleic <i>cis</i> -9-18:1
E	Elaidic <i>trans</i> -9-18:1
L	Linoleic <i>cis</i> -9, <i>cis</i> -12-18:2
Ln	Linolenic <i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-18:3
Ag-HPLC	Silver ion high performance liquid chromatography
NMR	Nuclear magnetic resonance
SFC	Solid fat content

The 1- and 3- positions on the glycerol backbone of the MAG, DAG and TAG molecules are assumed to be equivalent. Mention of trade names or commercial products in this (publication) is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.

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Introduction

Both the amounts of and specific structures of the triacylglycerol (TAG) present in the oil phase of a margarine or spread are considered responsible for both physical (spreadability, resistance to water/oil loss) and sensory (melting, graininess) properties. Thus cocoa butter (which

contains significant amounts of the symmetrical TAG isomers SOS, POS and POP), is a solid at room temperature, yet melts sharply at body temperature, and is thus highly prized as a confectionary fat. POP, due to its ability to form a variety of polymorphic compounds [1] and slow crystallization properties, is an important component of cocoa butter and palm oil. Interesterification of palm oil converts some of the naturally occurring POP to the non-symmetrical TAG isomer OPP, which crystallizes much more rapidly than POP. POP also tends to form large, coarse crystals (the β form) leading to graininess in emulsified spreads and shortenings [2, 3], while both EPP and PEP crystallize in the β' form, a more-desirable form for spreads and shortenings [4].

To better understand the interrelationship of TAG structures (symmetrical vs. non-symmetrical) and their contribution to the functional properties of fats, oils [5] or bakery shortenings [6], a number of symmetrical [tripalmitin (PPP), POP, PLP and PLnP] and non-symmetrical (OPP, EPP, LPP and LnP) TAG isomers were synthesized by esterification of the appropriate 1,3-DAG or 1(3)-MAG precursors, respectively [7, 8]—an extension of Kodali's synthesis [9]—and their melting/drop point and solid fat content values determined.

Experimental

Materials and Methods

Palmitic, elaidic, oleic, linoleic (L) and linolenic (Ln) fatty acids and 1(3)-monoacyl (-palmitin, -olein, -linolein and -linolenin) glycerols were purchased from Nu-Chek-Prep, Elysian, MN, USA. Sodium methoxide was from Harshaw Chem. Co. (Cleveland, OH, USA), *N,N'*-dicyclohexylcarbodiimide (DCCI) and *p*-toluenesulfonic acid from Sigma-Aldrich (St Louis, MO, USA), 4,4-dimethylaminopyridine (DMAP) from Eastman Fine Chemicals (Rochester, NY, USA) and Silica gel (60/200) from J.T. Baker Chemical Co. (Phillipsburg, NJ, USA). All solvents were either HPLC grade (acetone, acetonitrile, methanol) or ACS grade [petroleum ether (PE), carbon tetrachloride, ethyl ether (EE), toluene, benzene], and were used as received.

Silver Ion-HPLC

A Spectra-Physics P2000 solvent delivery system (Spectra-Physics Analytical, San Jose, CA, USA/now Thermo-Finnigan), a Rheodyne 7125 injector (Rheodyne Inc., Cotati, CA, USA) with a 20- μ L injection loop, and ELSD (Sedex Model 75; SEDERE, France) or an ISCO V4

Absorbance Detector (ISCO Inc., Lincoln, NE, USA) at a wavelength of 206 nm were utilized, with data collection via SS420X and ChromQuest 3.0 software (ThermoQuest Corp., San Jose, CA, USA). The ChromSpher[®] Lipids columns (4.6 mm I.D. \times 250 mm stainless steel; 5 micron particle size; silver ion impregnated) were purchased from Varian-Chrompack Int., (Middelburg, The Netherlands) and used as received.

Thin-layer Chromatography

Formation of the mono- or dipalmitoyl, oleoylglycerol intermediates and the final TAG were followed by TLC [7]. Samples (5–10 mg) were dissolved in 1.0 mL hexane and applied (ca. 10 μ L) to 1" \times 3" silica gel TLC [K6] plates (Whatman Inc., Clifton, NJ, USA). Eluting solvent: 80:20—hexane: ethyl ether (v/v; [11]); visualization by I₂ vapor or by spraying with 10% CuSO₄ in 8% H₃PO₄ solution/heating to 120 °C (hot plate).

Gas Chromatography/Chemical Purities

Chemical purities of the 1(3)-MAGs or 1,3-DAGs, and of the synthesized TAG were determined by gas chromatography after conversion (5% HCl in methanol) to FAMES [12]. A Varian 3400 Gas Chromatograph (Varian Instruments, Palo Alto, CA, USA) equipped with a 100 m \times 0.32 mm SP2380 (Supelco Inc., Bellefonte, PA, USA) capillary column, flame ionization detector and He as carrier gas (operating conditions: injector, 240 °C; split ratio, 100:1; oven temperature programmed from 155 to 220 °C at 3 °C/min with an initial hold of 15 min; detector, 280 °C) was utilized.

Acylglycerol Structures

The structural purities of the isolated or purchased MAG and DAG (after conversion to di- or monoacetate(s), respectively) starting materials [13] and of the synthesized TAG [14] were determined by Ag-HPLC [7]. Two Ag-HPLC columns were connected in series, and the solvent flow (isocratic conditions, 1.0% acetonitrile in hexane, 21 °C) standardized at 1.0 mL/min.

Drop Point

Drop points were determined utilizing a Mettler (Columbus, OH, USA) FP90 (incl. FP84 Dropping and Softening Point Module), by AOCS Official Method Cc 18–80 [15].

Percent Solids

Percent solids were determined by pulsed nuclear magnetic resonance (NMR). A Bruker Minispec NMR (Toronto, ON, Canada) was utilized at a temperature range from 10 to 65 °C, according to AOCS Official Method Cd 16-81 [15].

Syntheses

See Table 1 for the chemical and structural purities of final products.

Preparation of PPP

Palmitic acid (66.8 g, 0.25 mol) was combined with glycerol (7.3 g, 0.08 mol) and 0.7 g *p*-toluenesulfonic acid in a 250 mL, three-necked round-bottom flask fitted with an argon inlet and thermometer. The contents were stirred magnetically, under an argon atmosphere, and heated in an oil bath to 115 °C. Water which condensed on the flask walls during the reaction was removed by use of a heat gun. Reaction progress was measured by TLC. After 5 h, the reaction mixture was cooled and the solid residue dissolved in 150 mL PE and transferred to a glass column (5 cm × 60 cm) packed with 500 g Florisil. PPP was isolated by elution with 1.5 L of 10% EE in PE, and the solvents removed to yield 59.2 g (85%) of PPP.

Preparation of 1,3-Dipalmitin

Tripalmitin (44.5 g, 5.5×10^{-2} mol) and glycerol (2.84 g, 3.1×10^{-2} mol) were combined in a 250 mL round-bottom flask equipped with reflux condenser and argon inlet.

Table 1 Chemical and structural purities, drop points, and solids loss ranges of PPP, POP, OPP, PLP, LPP, EPP, PLnP, and LnPP

TAG	Purities ^a		Drop point (°C; Mettler)	Solids loss (by NMR)
	Chemical	Structural		
PPP	>99	>99	68.1	65–70
POP	98	>98	36.0	40–50
OPP	97	99	30.6	26.7–33
PLP	98	>97	26.0	21.1–26.7
LPP	97	99	29.3	26.7–33
EPP	97	98	46.1	40–50
PLnP	97	99	27.3	26.7–33
LnPP	96	99	30.0	26.7–33

^a All data are the means of duplicate determinations. Adapted from Ref. [15]

Sodium methoxide (0.26 g) was added and the magnetically stirred mixture was heated to 115 °C overnight. DAG formation was followed by TLC. (After 7 h, another 0.1 g of sodium methoxide was added.) After 24 h, the mixture was cooled to room temperature, dissolved in 20 mL benzene and eluted through a glass column (5 cm × 70 cm) packed with 200 g silica gel. The TAG (16.9 g) were eluted with 500 mL benzene, the DAG (19.0 g; ca. 40% yield) with 1.2 L 90:10 benzene: ether and the MAG/FA (4.8 g) with 1.7 L 100% ether (similar results were obtained when less-toxic toluene was substituted for benzene). A portion (14.4 g) of the DAG fraction was dissolved in 500 mL acetone, and the solution was slowly cooled to 5 °C and stored overnight. The crystals (6.5 g) were isolated by filtration through a cold Buchner funnel, and the DAG composition (conversion to the monoacetate/Ag-HPLC [13]) determined to be >99% 1,3-dipalmitoylglycerol.

Preparation of POP

POP was prepared following the method of Kodali et al. [9]. 1,3-Dipalmitoylglycerol (5.8 g, 1.0×10^{-2} mol) in 150 mL carbon tetrachloride (CCl₄) was transferred to a heat-dried, three-necked, 250 mL round-bottom flask equipped with a mechanical stirrer, thermometer and argon inlet. Oleic acid (3.16 g, 1.1×10^{-2} mol, 10% excess) in 10 mL of CCl₄ was added via syringe and the solution was heated to 30 °C in an oil bath. DMAP (1.22 g) was added in one portion followed by the dropwise addition of DCCI (1.6 g) over a 30-min period (precipitate noted), and the reaction was stirred under argon atmosphere for 3.5 h at 28 °C. The solution was then cooled to room temperature, the precipitate removed by vacuum filtration, and the solvents by rotary evaporator. The residue (10.3 g) was transferred with 20 mL PE to a glass column (2.5 cm × 70 cm) packed with 30 g silica gel, and eluted with 3 × 200 mL 5% EE in PE. Evaporation of the solvents yielded 7.0 g (84% yield) of POP.

Preparation of PLP

See “Preparation of POP.” 1,3-dipalmitoylglycerol (5.8 g, 1.0×10^{-2} mol, in 150 mL carbon tetrachloride) was esterified with L acid (3.13 g, 1.1×10^{-2} mol, 10% excess, in 10 mL of CCl₄), with DMAP (1.34 g) and DCCI (1.6 g in 10 mL CCl₄, added over 20 min). The solution was stirred for 2 h at 29 °C (2.3 g more L acid was added after 1 h), cooled, filtered and the solvents evaporated [TLC indicated incomplete esterification (and more L acid was added), but problem/low 70% yield may have been due to presence of water]. The residue (12.1 g) was purified by

elution (3×200 mL 5% EE in PE) through 60 g silica gel (2.5 cm \times 70 cm glass column) to yield PLP (6.0 g; 71% yield).

Preparation of PLnP

See “[Preparation of POP.](#)” 1,3-Dipalmitoylglycerol (5.5 g, 9.6×10^{-3} mol, 150 mL CCl_4) was esterified with Ln acid (3.11 g, 1.1×10^{-2} mol, 10% excess, in 10 mL of CCl_4). DMAP (1.22 g) and DCCI (1.6 g in 5 mL CCl_4 , dropwise over a 30 min) were added and the reaction mixture stirred at 30 °C for 2.5 h. After cooling to room temperature, the precipitated solid was removed by vacuum filtration and the solvents removed by rotary evaporation. The residue (10.9 g) was purified by elution (4×200 mL portions 5% EE in PE) through 60 g silica gel (2.5 cm \times 70 cm glass column) to yield 6.9 g (87% yield) of PLnP.

Preparation of OPP

See “[Preparation of POP.](#)” PPO was prepared by esterification of 1-monoolein (4.0 g, 1.12×10^{-2} mol, in 180 mL CCl_4) with palmitic acid (6.4 g, 2.36×10^{-2} mol, 10% excess, in 10 mL CCl_4), in 350 mL round-bottom flask in the presence of DMAP (1.1 g) and DCCI (6.02 g in 15 mL CCl_4). After stirring at 33 °C for 2.5 h, the solution was cooled, filtered and the solvents evaporated. The residue (12.9 g) was eluted (4×200 mL 5% EE in PE) through 60 g silica gel (5 cm \times 40 cm glass column) to yield 8.1 g (87% yield) of OPP.

Preparation of EPP

See “[Preparation of POP.](#)” 1(3)-monoelaidin (3.1 g, 8.7×10^{-3} mol, in 140 mL CCl_4) was esterified with palmitic acid (5.1 g, 1.95×10^{-3} mol, 10% excess, in 10 mL of CCl_4). DMAP (1.06 g, 8.2×10^{-3} mol, one batch) and DCCI (4.2 g, dropwise over 30 min, precipitate formation noted) were added. The reaction was stirred for 2 h at 39 °C. After cooling to room temperature, the precipitate was removed by vacuum filtration, and the solvents removed by rotary evaporator. The residue (10.1 g) was eluted (5×200 mL 5% EE in PE) through 60 g silica gel (2.5 cm \times 70 cm glass column), to yield EPP (6.5 g, 89% yield).

Preparation of LPP

See “[Preparation of POP.](#)” 1(3)-Monolinolein (4.0 g, 1.13×10^{-2} mol) in 100 mL CCl_4 /250 mL round-bottom

flask was esterified with palmitic acid (6.32, 2.47×10^{-2} mol, 10 mL CCl_4), DMAP (1.4 g) and DCCI (5.64 g in 15 mL CCl_4 , over 30 min) and stirred under inert gas at 33 °C for 2.5 h. The solution was cooled, filtered and the solvents evaporated. The residue (12.5 g) was purified by elution (4×200 mL 5% EE in PE) through 60 g silica gel (2.5 cm \times 70 cm glass column) to yield 8.5 g (89% yield) of LPP.

Preparation of LnPP

See “[Preparation of POP.](#)” 1-Monolinolein (4.97 g, 1.41×10^{-2} mol, in 100 mL CCl_4) in a 350 mL round-bottom flask, was esterified with palmitic acid (8.02 g, 3.13×10^{-2} mol, 10 mL CCl_4). DMAP (1.73 g) and DCCI (7.02 g, 5 mL CCl_4 , batchwise over 20 min) were added and the solution stirred under argon gas at 29 °C for 2.5 h. The solution was cooled, filtered, and the solvents evaporated. The residue (15.3 g) was purified by elution (4×150 mL 5% EE in PE) through 60 g silica gel (2.5 cm \times 70 cm glass column) to yield 10.5 g (88% yield) of LnPP.

Analyses

Chemical and structural purities, drop melting points (Mettler) and solid loss ranges of PPP, POP, OPP, PLP, LPP, EPP, PLnP, and LnPP are listed in Table 1, and the percent solids by NMR in Table 2.

Results and Discussion

Multi-gram (4–6 g) quantities of a variety of symmetrical and non-symmetrical isomers can be readily prepared by

Table 2 Percent solids by NMR (10–65 °C)

TAG	Solids (%) at temperature (°C)						
	10	21.1	26.7	33.3	40	60	65
PPP	99.5	99.5	99.1	99.1	98.6	98.1	75.0
POP	98.8	97.9	95.1	81.1	9.2	0.0	0.0
OPP	95.4	93.5	75.0	0.3	0.0	0.0	0.0
PLP	86.6	78.2	0.4	0.1	0.0	0.0	0.0
LPP	85.4	80.8	59.3	0.0	0.0	0.0	0.0
EPP	99.2	99.0	98.4	98.0	94.0	0.0	0.0
PLnP	86.8	67.8	25.2	0.4	0.0	0.0	0.0
LnPP	86.3	82.6	61.1	0.0	0.0	0.0	0.0

All data are the means of duplicate determinations. Adapted from Ref. [15]

esterification of the appropriate, thermodynamically more-stable 1,3-DAG or 1(3)-MAG, respectively. POP, PLP and PLnP were prepared by esterification of 1,3-dipalmitoylglycerol (1,3-diP-DAG) with oleic, L or Ln acid, respectively. The diP-DAG precursors were readily synthesized by partial glycerolysis of PPP [10], the DAG fraction (ca. 80% 1,3- and 20% 1,2-di-DAG isomer) separated by silica gel chromatography, and the 1,3-diP-DAG component isolated in 99+% chemical and structural purity by low-temperature crystallization from acetone. The thermodynamically less-stable (and, if commercially available, significantly more expensive) 1,2P-DAG, present at only 20–25% in the original diP-DAG fraction, could be isolated in purities of ca. 85% [16], but further purification/removal of the 1,3-DAG “impurities” by repeated crystallizations, resulted in losses of >50% of the desired 1,2-isomer. Utilization of the less-pure 1,2P-DAG precursor for preparation of non-symmetrical TAG isomers such as PPO, PPL or PPLn required extensive, and time-consuming, purification of the final product by semi-preparative silver ion TLC or HPLC. We found Ag-HPLC to be a rapid and reproducible method to analyze the final structured TAG, with a detection limit of <0.5% for the “undesired” isomer [8].

A similar situation was noted during preparation and isolation of the 1(3)P-MAG. While the 16:0, 18:0 and 18:1-MAG isomers could be readily isolated, the more highly unsaturated (18:2, 18:3, etc.) 1(3)-MAG isomers were more difficult to prepare in the quantities and structural purities (>98%) desired for synthesis of such non-symmetrical TAG isomers as PPL and PPLn. The more-stable 1(3)-MAGs, like the 1,3-DAG analogues, were usually readily available in multi-gram quantities from commercial sources. The 2-MAG isomers, like the 1,2-DAG, were also very difficult to synthesize and were often not commercially available, except by “special (and expensive) synthesis.”

The chemical and structural purities, drop points and solids losses of the TAGs synthesized in this study are listed in Table 1, and the percent solids values (NMR; 10–65 °C) in Table 2. All TAGs were found to be at least 97% chemically and structurally (ABA vs. BAA) pure. Melting points were determined by Mettler dropping point. Insertion of oleic or elaidic acid into the molecule lowered the melting point of PPP by ca. 47% for the symmetrical POP, 55% for OPP, but only 32% for EPP. Our NMR data shows that PPP, POP, OPP and EPP are essentially solids at 10 °C. In general, the NMR data indicate a high degree of purity, since the solid fat values approach 0 at temperatures near the Mettler melting points.

While the melting points of POP, PLP, PLnP, OPP, PEP and EPP have been reported in the literature [17–23], the values for EPP, PLnP and LnPP have not. OPP reportedly melts at 34–35.2 °C [24]. (PPO, unlike POP and most TAG

isomers, does not have a β crystalline form [24, 25]; its most-stable form is β' . Hydrogenation of palm oil is reported to improve its crystallization and melt properties due to conversion of POP to the elaidenized form, PEP. The reported [26] melting points of POP range from 35.1 to 38.5 °C, which is in agreement with our data of 36 °C (Mettler dropping point). Our drop point value for EPP was ca. 46 °C, (lower than the value of 50.2 °C obtained by Wesdorp [23]), compared to a value of 53.5 °C for the symmetrical PEP isomer [22]. Care must therefore be utilized when applying Official or Standard Methods to the characterization of structured TAG, whether as pure samples, mixtures or in commercial formulations.

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