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Two-Step Production of Oil Enriched in Conjugated Linoleic Acids and Diacylglycerol

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Abstract A two-step process was used to produce diacylglycerol-enriched structured lipid that contained mainly *c*9,*t*11 and *t*10,*c*12 isomers of conjugated linoleic acids (CLA). First, a structured triacylglycerol (TAG) was synthesized by lipase-catalyzed acidolysis of corn oil with CLA. This structured triacylglycerol contained 30.4 mol% CLA with 45.5% of the CLA mostly located at *sn*-1,3 positions of the glycerol backbone. Then, lipase-catalyzed glycerolysis was conducted between structured triacylglycerol and glycerol to produce diacylglycerol-enriched structured lipid. The final product contained 6.8% monoacylglycerol, 31.5% diacylglycerol and 61.1% TAG after 48 h reaction. The selected chemical (fatty acid composition, the content of mono-, di-, and triacylglycerol in the reaction product) and physical properties (melting profile) were determined by hihg-performance liquid chromatography (HPLC), gas chromatography (GC), and differential scanning calorimetry (DSC).

Keywords Structured lipid · Glycerolysis · Diacylglycerols · Conjugated linoleic acids · Lipase-catalyzed reaction

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Introduction

Lipase-assisted modification of lipids is a useful way to improve their physicochemical and nutritional properties. Functional fatty acids can be incorporated into specific positions of the triacylglycerol (TAG) molecule through lipase-catalyzed reaction [1–6]. For example, conjugated linoleic acids (CLA) that possess several health benefits [7–9] have been used for the production of such modified TAG, referred to as structured lipids (SL).

Monoacylglycerols (MAG) and diacylglycerols (DAG) are important emulsifiers inthefood, cosmetic, and pharmaceutical industries [10]. Recently, a dietary lipid containing increased levels (about 80% or above) of DAG was introduced in Japan and USA. Such a lipid was considered to be metabolized differently fromconventional TAG. Recent research showed that a diet containing DAG reduced body weight by an average of 3.6% and fat mass by 8.3% in overweight or obese people because DAG tends to be oxidized for energy rather than stored as fat [11].

Conventionally, MAG and DAG are prepared by chemical glycerolysis of edible fat and oils with excess amount of glycerol at high temperatures [10]. The chemical synthesis under high temperature is sometimes disadvantageous because colored and odoriferous polymers are formed after the reaction [12, 13]. To overcome such problems, enzymatic reactions involving several approaches have been investigated. For example, TAG was converted to MAG and DAG by controlled lipase-catalyzed hydrolysis [14]. Yang et al. [15] synthesized MAG and DAG through lipase-catalyzed glycerolysis of butter oil. Lipase-catalyzed direct esterification between fatty acids and glycerol would

generate water that must be controlled so that complete hydrolysis is prevented. However, generation of water could be avoided through lipase-catalyzed glycerolysis between TAG and glycerol.

In this study, DAG and MAG were produced by lipase-catalyzed reaction, in which CLA was incorporated into the DAG and MAG. For this purpose, SL was first produced from the lipase-catalyzed acidolysis between corn oil and CLA as free fatty acids. Then, glycerolysis was conducted between SL and glycerol to produce MAG and DAG containing CLA. We report the synthesis and physicochemical properties of DAG-enriched SL-containing CLA.

Experimental Procedures

Materials

Corn oil was purchased from CJ Co. (Seoul, Korea). CLA fatty acid mixture (70CLA^{TM}) produced from safflower oil was provided by Livemax Co. (Sungnam, Korea). The main CLA isomers of 70CLA^{TM} were *cis*-9, *trans*-11 CLA (30.1%), and *trans*-10, *cis*-12 CLA (30.6%). Other fatty acids were found as follows: $C_{16:0}$ (7.2%), $C_{18:0}$ (2.7%), $C_{18:1}$ (*c*, 17.7%), $C_{18:1}$ (*t*, 1.9%), $C_{18:2}$ (6.7%), and other CLA isomers (3.2%). Lipozyme RM IM (lipase from *Rhizomucor miehei* immobilized on a macroporous anion exchange resin) was obtained from Novozymes, Inc. (Bagsvaerd, Denmark). All solvents were HPLC grade and purchased from J.T. Baker (Phillipsburg, USA). Pancreatic lipase and bis(trimethylsilyl) trifluoroacetaminde (BSTFA) were purchased from Sigma–Aldrich Inc. (St Louis, USA).

Production of SL

Production of SL was performed in a 250-mL screw-capped Erlenmeyer flask in which corn oil (30 g), CLA (28.9 g) at the 1:3 molar ratio, and 10% Lipozyme RM IM (5.89 g) were mixed. Flasks were placed in a shaking water bath at 175 revolutions per minute (rpm) and incubated at 55 °C for 24 h. Synthesized SL from corn oil and CLA were filtered under vacuum to recover lipases. Excess free fatty acids were deacidified by distillation at 210 °C and 0.1 torr for 1 h followed by alkali deacidification. Alkali deacidification was conducted as follows. Each 20 g sample was placed in a separating funnel and 120 mL of 0.5 N KOH (20% in ethanol), 4–5 drops of phenolphthalein (1% in ethanol) and 250 mL *n*-hexane were added. The water phase (red color) was removed and the *n*-hexane phase was collected. After passing through an anhydrous sodium sulfate column, *n*-hexane was removed with rotary evaporator and nitrogen gas. The production was duplicated.

Production of DAG-Enriched Oil from SL

A mixture of alkali-deacidified SL (400 g), glycerol (20 g) at the 1:2 molar ratio and Lipozyme RM IM lipase (10 g, based on the SL weight) was placed in a 1-L stirred tank batch-type reactor with no solvent added and incubated for 48 h at 60 °C. A semicircular-shaped (9 cm diameter and 3.2 cm height) stirring blade with speed controller was used to mix the reactants. The mixing speed was 200 rpm. The dimensions of the water-jacketed reactor tank were 11 cm internal diameter and 15 cm height. The blade was placed at a distance of 1 cm from the bottom of the reactor. The temperature of reactor was maintained by circular water heater. Samples were taken at the designated reaction times for analysis. After 48 h reaction, reactant was filtered under vacuum to recover lipases from the reaction mixture, and *n*-hexane (100 mL) added. Then, it was centrifuged (3,000 rpm) to separate unreacted glycerol. The upper *n*-hexane phase was appliedrepeatedly to an anhydrous sodium sulfate column. Excess *n*-hexane was then removed with a rotary evaporator and nitrogen gas. The production was duplicated.

Hydrolysis by Pancreatic Lipase and Fatty Acid Analysis

To study the positional distribution of fatty acids, each sample (5 mg) was placed in a test tube and 5 mL Tris-HCl buffer (pH 7.6) 1.25 mL bile salt (0.05%, w/v), 0.5 mL calcium chloride (2.2%, w/v), and 5 mg pancreatic lipase were mixed. After incubating at 37 °C for 3 min, the mixture was agitated vigorously for 30 s. The hydrolytic product was extracted with 2 mL diethyl ether, dried over anhydrous sodium sulfate column and concentrated by nitrogen gas. The hydrolytic products were then separated by silica-gel-impregnated thin-layer chromatography (TLC) using *n*-hexane: diethyl ether: acetic acid (50:50:1, v/v/v) as a developing solvent. The bands corresponding to MAG was scraped for methylation. For the determination of the fatty acid composition, 6% sulfuric acid in methanol (3 mL, v/v) was used to prepare fatty acid methyl esters in the presence of heptadecanoic acid as an internal standard (50 μL, 1 mg/mL *n*-hexane). The

mixture was placed in a dry oven for 1 h at 70 °C. Hexane (2 mL) was added to extract fatty acid methyl esters. The hexane phase was dried over an anhydrous sodium sulfate column and placed in a Ggas chromatography (GC) vial.

Gas Chromatography (GC)

A Hewlett–Packard 6890 gas chromatograph (Avondale, PA, USA) with auto-injector and flame-ionization detector was used for fatty acid methyl ester analysis. A Supelco fused-silica capillary column (SP-Wax, 60 m × 0.25 mm i.d.; Bellefonte, PA, USA) was used. The temperature was held at 100 °C for 5 min and increased to 220 °C for 30 min at the rate of 4 °C/min. Nitrogen was used as the carrier gas and the flow rate at inlet was 52 mL/min with split mode 50:1. The temperatures of the injector and detector were 250 and 260 °C, respectively.

High-Performance Liquid Chromatography (HPLC)

Reaction product was filtered with a Whatman PTFE Syringe filter and diluted with *n*-hexane for NP-HPLC or acetone for RP-HPLC analysis. The HPLC system was a Younglin SP 930D dual pump (Anyang, Korea). Sedex 75 evaporative light scattering detector (Alfortvill, France) was operated at 40 °C with nitrogen as a nebulizing gas at a pressure of 2.2 bar. The area of each peak was integrated by Autocho-2000 software (Anyang, Korea). For NP-HPLC, Hypersil®BDSCPS 5 μm (4.6 × 250 mm column, USA) was used. A binary solvent system of *n*-hexane and methyl-*t*-butyl ether with each solvent fortified with 0.4% acetic acid was the mobile phase at a flow rate of 1 mL/min. The gradient program was used as follow: 0–5 min, 100% *n*-hexane; 5–15 min, 100–20% *n*-hexane; 15–17 min, 20% *n*-hexane; 17–17.1 min, 20–100% *n*-hexane; 17.1–27 min, 100% *n*-hexane.

High-Temperature Gas Chromatography

To measure the content of glycerol in the product, GC Model M600D (Younglin, Korea) equipped with a DB1-HT methyl-silicone capillary column (15 m × 0.32 mm i.d., film thickness 0.1 μm; J&W Scientific, USA) and an FID was used. A mixture of 100 mg sample and 100 μL BSTFA was placed at room temperature for 20 min. The trimethylsilyl derivative was diluted in 10 mL *n*-hexane and analyzed. Injector and detector temperature was 380 °C. Helium was used as a carrier gas at a flow rate of 3 mL/min. The thermal program was described by Lee et al. [16].

Differential Scanning Calorimetry

The solidification and melting profiles were determined with a DSC 2010 differential scanning calorimeter (TA Instruments, New Castle, USA). The baseline was obtained with an empty aluminum pan. Each sample (8 ± 0.1 mg) was accurately weighed for DSC analysis. The instrument temperature was increased to 80 °C and after 10 min at this temperature the cooling curve was obtained by cooling at 10 °C/min to –60 °C. After holding for 10 min at –60 °C, the temperature was returned to 80 °C at 5 °C/min [17].

Results and Discussion

Chemical Structural Properties

The fatty acid compositions of corn oil, SL and SL-DAG are shown in Table 1. For acidolysis, alkali deacidification removed free fatty acids from the product as the acid value of SL was below 0.3, and the yield of acidolysis reaction achieved 84.3% based on the weight of deacidified SL to corn oil (data not shown). Naturally, vegetable oils are rich in unsaturated fatty acids that tend to locate mainly at the *sn*-2 position in TAG molecule, while the saturated fatty acids are located at *sn*-1 and *sn*-3 positions [18]. Similar result was obtained in this study with corn oil. After acidolysis of corn oil with CLA, the fatty acid composition of SL was different from corn oil as the contents of $C_{18:2}$ and $C_{18:1}$, which were the main fatty acids of corn oil, decreased to 32.3 and 26.6%, respectively. The content of total CLA, which was not found in corn oil, increased to 30.4%. Among the CLA isomers, *c*9,*t*11 and *t*10,*c*12 CLA were predominantly present in SL and incorporated CLA (45.5%) were mostly found at the *sn*-1,3 positions (Table 1). After 48 h reaction, CLA was not found at the *sn*-2 position in SL and SL-DAG, suggesting that acyl migration did not occur significantly under each reaction condition with 1,3-positional Lipozyme RM IM lipase. Positional fatty acid compositions of SL-DAG were similar to that of SL.

The SL-DAG reaction product was separated by TLC to obtain purified MAG, DAG and TAG molecules, and the changes in the fatty acid composition with time were determined (Table 2). During the 48 h reaction, the proportion of CLA incorporated into

Table 1 Fatty acid compositions of corn oil, structured lipid (Sl) and diacylglycerol-enriched structured lipid (SL-DAG)

	Corn oil			SL[a]			SL-DAG[b]		
	sn-2	*sn*-1,3	Total	*sn*-2	*sn*-1,3	Total	*sn*-2	*sn*-1,3	Total
Palmitic acid, $C_{16:0}$	2.7 ± 0.1	9.5 ± 0.1	13.8 ± 0.1	5.9 ± 0.1	9.5 ± 0.2	8.3 ± 0.1	7.5 ± 0.2	8.8 ± 0.1	8.4 ± 0.2
Palmitoleic acid, $C_{16:1}$	ND	0.2 ± 0.1	0.2 ± 0.1	ND	0.2 ± 0.1	0.1 ± 0.1	ND	ND	ND
Stearic acid, $C_{18:0}$	1.1 ± 0.1	1.7 ± 0.1	1.9 ± 0.1	1.0 ± 0.0	1.8 ± 0.1	1.6 ± 0.1	1.7 ± 0.1	1.6 ± 0.1	1.6 ± 0.1
Oleic acid, $C_{18:1}$	36.3 ± 0.2	38.7 ± 0.8	32.7 ± 0.5	41.0 ± 0.7	19.6 ± 0.1	26.6 ± 0.1	45.4 ± 0.2	17.9 ± 0.3	27.1 ± 0.4
Linoleic acid, $C_{18:2}$	58.7 ± 0.1	48.9 ± 1.0	51.2 ± 0.2	50.8 ± 0.5	23.0 ± 0.2	32.3 ± 0.3	44.8 ± 0.5	25.6 ± 0.4	31.9 ± 0.1
Linolenic acid, $C_{18:3}$	1.2 ± 0.1	1.0 ± 0.1	0.2 ± 0.1	1.3 ± 0.1	0.4 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	0.7 ± 00
*c*9,*t*11 CLA	ND	ND	ND	ND	21.0 ± 0.5	14.0 ± 0.1	ND	20.8 ± 0.2	13.9 ± 0.3
*t*10,*c*12 CLA	ND	ND	ND	ND	21.4 ± 0.1	14.3 ± 0.1	ND	21.4 ± 0.1	14.2 ± 0.1
*c*9,*c*11; *t*11,*t*13 CLA	ND	ND	ND	ND	1.6 ± 0.1	1.1 ± 0.1	ND	1.6 ± 0.1	1.1 ± 0.1
*t*8,*t*10; *t*9,*t*11; *t*10,*t*12 CLA	ND	ND	ND	ND	1.5 ± 0.1	1.0 ± 0.2	ND	1.6 ± 0.1	1.1 ± 0.1
Total CLA	ND	ND	ND	ND	45.5	30.4	ND	45.4	30.3

Values are the means of three samples

ND not detected, *sn*-2 the fatty acid at *sn*-2 position of glycerol backbone, *sn*-1,3 the fatty acids at *sn*-1,3 position of the glycerol backbone

[a] Produced from acidolysis reaction of corn oil and CLA. The detailed procedure was described in Experimental Procedures

[b] Produced from glycerolysis reaction of SL and glycerol. The detailed procedure was described in Experimental Procedures

MAG and DAG molecules ranged from 12.4 to 34.3 mol%. The total amounts of incorporated CLA were higher in MAG than in DAG. The proportions of CLA were gradually increased during 48 h reaction while reductions in $C_{18:1}$ and $C_{18:2}$ were observed for each lipid class (MAG, DAG, TAG). After 48 h, DAG and MAG containing 28.2 and 34.3% CLA were obtained (Table 2).

The reaction mixtures from glycerolysis were obtained at the designated reaction times for NP-HPLC

Table 2 Fatty acid composition of monoacylglycerol (MAG), diacylglycerol (DAG) and triacylglycerol (TAG) molecules in diacylglycerol-enriched structured lipid (SL-DAG) during the 48 h reaction

Reaction time (h)		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3n-3}$	*c*9,*t*11 CLA	*t*10,*c*12 CLA	*c*9,*c*11; *t*11,*t*13 CLA	*t*8,*t*10; *t*9,*t*11; *t*10,*t*12 CLA	Total CLA
1.5	MAG	9.4 ± 0.3	2.7 ± 0.1	34.2 ± 0.2	33.0 ± 0.8	ND	10.4 ± 0.8	10.3 ± 0.2	ND	ND	20.7
	DAG	14.5 ± 0.1	2.6 ± 0.1	33.9 ± 0.1	32.8 ± 0.1	0.8 ± 0.1	5.6 ± 0.1	5.9 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	15.4
	TAG	8.7 ± 0.1	1.5 ± 0.1	33.7 ± 0.1	35.1 ± 0.1	0.8 ± 0.1	8.5 ± 0.1	8.7 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	21.0
3	MAG	11.1 ± 0.1	2.6 ± 0.1	33.2 ± 0.8	32.0 ± 0.1	ND	10.0 ± 0.1	11.1 ± 0.6	ND	ND	21.1
	DAG	13.2 ± 0.1	2.8 ± 01	38.3 ± 0.3	32.7 ± 0.1	0.6 ± 0.1	4.5 ± 0.1	5.1 ± 0.1	1.4 ± 0.2	1.4 ± 0.1	12.4
	TAG	9.8 ± 0.4	1.8 ± 0.1	30.9 ± 1.7	34.2 ± 0.1	0.7 ± 0.4	9.7 ± 0.9	10.1 ± 0.8	1.5 ± 0.1	1.3 ± 0.2	22.6
4.5	MAG	12.1 ± 0.3	2.7 ± 0.2	30.4 ± 0.1	30.9 ± 0.1	ND	12.0 ± 0.4	11.9 ± 0.2	ND	ND	24.0
	DAG	12.0 ± 0.2	2.6 ± 0.1	35.7 ± 0.3	32.7 ± 0.1	0.6 ± 0.1	6.5 ± 0.1	7.0 ± 0.1	1.8 ± 0.1	1.1 ± 0.1	16.4
	TAG	8.5 ± 0.4	1.6 ± 0.1	28.3 ± 0.6	34.2 ± 0.2	0.8 ± 0.1	11.6 ± 0.2	12.0 ± 0.3	1.6 ± 0.1	1.4 ± 0.1	26.6
18	MAG	10.1 ± 0.3	2.3 ± 0.1	28.6 ± 0.4	29.6 ± 0.8	0.9 ± 0.2	11.8 ± 0.3	12.1 ± 0.5	2.4 ± 0.4	2.2 ± 0.3	28.5
	DAG	9.5 ± 0.5	2.1 ± 0.1	31.7 ± 0.4	33.5 ± 0.4	0.6 ± 0.1	9.5 ± 0.3	10.0 ± 0.3	1.7 ± 0.1	1.4 ± 0.1	22.6
	TAG	8.6 ± 0.1	1.6 ± 0.1	27.3 ± 0.7	34.0 ± 0.2	0.7 ± 0.1	12.2 ± 0.6	12.5 ± 0.5	1.7 ± 0.1	1.4 ± 0.1	27.8
24	MAG	9.0 ± 0.2	1.9 ± 0.1	26.3 ± 0.2	29.1 ± 1.6	4.0 ± 0.1	12.0 ± 0.5	12.6 ± 0.3	2.4 ± 0.4	2.7 ± 0.1	29.7
	DAG	8.9 ± 0.1	1.9 ± 0.1	28.3 ± 0.1	31.9 ± 0.0	0.8 ± 0.1	11.3 ± 0.2	11.4 ± 0.1	2.3 ± 0.1	3.2 ± 0.1	28.2
	TAG	8.5 ± 0.1	1.6 ± 0.1	27.6 ± 0.1	33.4 ± 0.1	0.7 ± 0.1	12.0 ± 0.1	12.0 ± 0.1	1.9 ± 0.1	2.3 ± 0.1	28.2
32	MAG	8.0 ± 0.2	2.2 ± 0.1	28.7 ± 0.7	30.0 ± 0.7	0.8 ± 0.1	12.9 ± 0.3	13.3 ± 0.4	2.8 ± 0.3	1.3 ± 0.3	30.3
	DAG	8.8 ± 0.2	1.9 ± 0.1	29.3 ± 0.4	32.7 ± 0.1	0.7 ± 0.1	11.1 ± 0.3	11.3 ± 0.3	2.2 ± 0.1	2.0 ± 0.1	26.6
	TAG	8.4 ± 0.2	1.6 ± 0.1	27.8 ± 0.1	34.1 ± 0.3	0.8 ± 0.1	11.7 ± 0.1	11.9 ± 0.2	1.9 ± 0.1	1.8 ± 0.2	27.3
48	MAG	5.7 ± 0.8	1.8 ± 0.2	26.5 ± 1.3	30.7 ± 0.3	1.0 ± 0.2	13.9 ± 1.2	14.2 ± 1.2	3.4 ± 0.1	2.8 ± 0.2	34.3
	DAG	7.0 ± 0.4	1.9 ± 0.1	28.9 ± 0.3	33.5 ± 0.1	0.5 ± 0.2	11.4 ± 0.1	11.6 ± 0.1	2.5 ± 0.1	2.7 ± 0.1	28.2
	TAG	7.3 ± 0.1	1.6 ± 0.1	28.3 ± 0.1	34.0 ± 0.3	0.8 ± 0.1	11.6 ± 0.1	11.7 ± 0.2	2.1 ± 0.1	2.6 ± 0.1	28.0

SL-DAG was produced from glycerolysis reaction of SL and glycerol. The detailed procedure was described in Experimental Procedures. Values are the means of three samples. For other abbreviations see Table 1

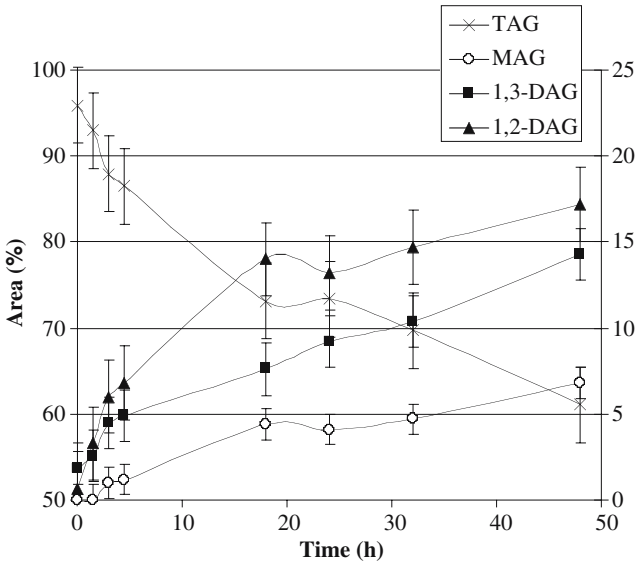

Fig. 1 The composition (*area%*) of triacylglycerol (*TAG*); 1,2-diacylglycerol (*1,2-DAG*); 1,3-diaylglycerol (*1,3-DAG*) and monoacylglycerol (*MAG*) at the designated time during the glycerolysis reaction. MAG (*circle*), 1,3-DAG (*filled square*), 1,2-DAG (*filled triangle*), TAG (cross)

analysis (Fig. 1); and the amounts of newly produced molecules (1,2-DAG, 1,3-DAG and MAG) determined. The peak area percentage for the produced DAG and MAG increased with prolonged reaction times, resulting in a concomitant reduction in TAG during the reaction. During the glycerolysis reaction between TAG and glycerol, different types of reaction could occur. First, 1 mol of TAG and 1 mol of glycerol would be consumed to produce 1 mol of MAG and DAG (TAG + G ⇄ MAG + DAG). Second, 1 mol of TAG with 1 mol of newly produced MAG (from TAG + G) could produce 2 mol of DAG (TAG + MAG ⇄ 2 DAG). Third, the newly produced 1 mol of DAG (from TAG + G ⇄ MAG + DAG or TAG + MAG ⇄ 2 DAG) could produce 2 mol of MAG with 1 mol of glycerol without consuming TAG (DAG + G ⇄ 2 MAG) [19, 20]. In this case, the substrate molar ratio of TAG to glycerol was 2:1. Based on stepwise production, this ratio may be desirable for maximizing the production of DAG desired in this study. In fact, after glycerolysis between TAG and glycerol, the product must be a mixture of MAG, DAG, unreacted glycerol, and unreacted TAG with free fatty acids. Unreacted glycerol was removed almost completely from the SL-DAG by using centrifugation since the glycerol content was 0.6% as determined by high-temperature GC (data not shown). After glycerolysis, the SL-DAG consisted of 6.8% MAG, 31.5% DAG (14.2% of 1,3-DAG, 17.2% of 1,2-DAG), and 61.1% TAG.

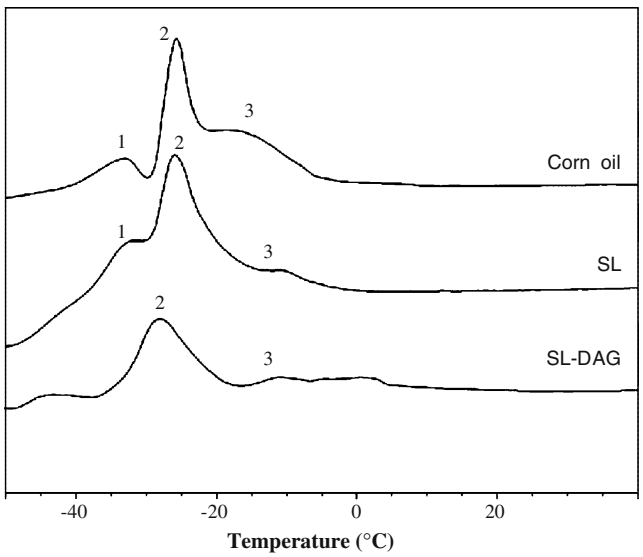

Fig. 2 Differential scanning calorimetry thermograms of corn oil, structured lipid (*SL*) and diacylglycerol-enriched structured lipid (*SL-DAG*). The peak positions 1–3 of the thermogram are discussed in the text

Melting Properties by DSC

In Fig. 2, the melting profile of corn oil showed three endothermic peaks with maxima at –33.3, –25.7 and –14.5 °C. A similar pattern of thermogram was obtained in SL except that the area of the broad peak (number 3) decreased. This would be explained by the incorporation of CLA in SL in which the content of total unsaturated fatty acid was increased. When olive oil was transesterified with CLA (21.8% incorporation) the crystallization temperature was shifted to a lower temperature [21]. In SL-DAG, peak number 2 was the main peak with a maximum at –28.2 °C, and the melting curve shifted to a lower temperature compared to that of corn oil and SL. Because SL and SL-DAG showed a similar fatty acid composition, the presence of DAG in SL-DAG product may cause a change in the melting properties. Oh et al. [22] reported that the presence of DAG containing unsaturated fatty acid in TAG reduces the area of melting peaks, shifting them to a lower temperature. In our result, the shifting of the peak to lower temperature with reducing peak area was also observed in SL-DAG, suggesting that such changes were occurred due to the presence of DAG in the reaction product.

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