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Melting properties of some structured lipids native to high stearic acid soybean oil

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RESUMEN

Propiedades de fusión de algunos lípidos estructurados procedentes del aceite de soja con alto contenido en ácido esteárico.

Se sintetizaron algunos lípidos estructurados procedentes del aceite de soja con alto contenido en ácido esteárico y sus propiedades físicas se determinaron por resonancia magnética nuclear pulsada (NMR), punto de goteo Mettler y calorimetría diferencial de barrido (DSC). Se sintetizaron 1,3 diestearo-2-oleina (SOS), 1,3 diestearo-2-linoleina (SLS) y 1,3 diestearo-2-linolenina (SlnS) a partir de 1,3 diacilgliceroles y de los ácidos grasos adecuados puros. Las determinaciones de NMR pulsada en el rango de temperaturas 10-50°C mostraron que los triacilgliceroles simétricos (SUS: donde S = esteárico, U = oleico, linoleico o linolénico) funden a mayor temperatura y más bruscamente, todos presentan altos contenidos en sólidos a todas las temperaturas hasta los 33.3°C, estando completamente fundidos a sólo unos pocos grados por encima. Los puntos fusión Mettler de SOS, SLS y SlnS fueron 44.1, 37.9 y 36.5°C respectivamente. Los calores de fusión de los triacilgliceroles estructurados determinados por DSC resultaron del orden de 29-32 cal/gm frente a 45 cal/gm del SSS. Se calcularon los calores de fusión también mediante las determinaciones de los puntos de goteo Mettler como mezclas con aceite de soja y mostraron una buena concordancia con los datos DSC.

PALABRAS-CLAVE: Aceite de soja - Calor de fusión - Calorimetría diferencial de barrido - Lípidos estructurales - Punto de goteo Mettler - Resonancia magnética nuclear.

SUMMARY

Melting properties of some structured lipids native to high stearic acid soybean oil.

A number of structured lipids native to high stearic acid soybean oil were synthesized and their physical properties were determined by pulsed nuclear magnetic resonance (NMR), Mettler dropping point and differential scanning calorimetry (DSC). 1,3 Distearo-2-olein (SOS), 1,3 distearo-2-linolein (SLS) and1,3 distearo-2-linolenin (SlnS) were synthesized from pure 1,3 diacylglycerols and the appropriate fatty acid. Pulsed NMR determinations over the temperature range 10-50°C showed that the symmetrical triacylglycerols (SUS: where S = stearic, U = oleic, linoleic or linolenic) are high and sharply melting materials, all showing substantial amounts of solids at temperatures up to 33.3°C, yet are completely melted at only a few degrees higher. Mettler dropping points for SOS, SLS and SlnS were 44.1, 37.9 and 36.5°C respectively. The heats of fusion for the structured triacylglycerols were determined by DSC and shown to be of the order 29-32 cal/gm compared to 45 cal/gm for SSS. The heats of fusion were also calculated from Mettler dropping point determinations as admixtures with soybean oil and showed consistent agreement with the DSC data.

KEY-WORDS: Differential scanning calorimetry - Heats of fusion - Mettler dropping point - Nuclear magnetic resonance - Soybean oil - Structured lipids.

1. INTRODUCTION

During the past decade a number of structurally modified soybean oils high in saturated acids have been introduced (Lui 1999, List *et al.* 1996, List *et al.* 1997). In their natural state, these oils exhibit melting points about 15°C lower than hydrogenated oils used in spreads and they lack sufficient solids at temperatures above 10°C (i.e. 21.1-33.3°C). This work was undertaken to characterize the physical properties of some structured lipids native to high stearic acid soybean oil.

2. MATERIAL AND METHODS

Stearic (S), oleic (O), linoleic (L) and linolenic (Ln) acids were purchased from Nu-Chek-Prep, Elysian, MN and were found 100% pure after conversion to methyl esters and analysis by gas chromatography. The symmetrical triacylglycerols, SOS, SLS and SlnS, were synthesized from 1,3-distearyl glycerol according to Kodali (1987). SOS, SLS and SlnS showed purities of 98.4, 100 and 100% respectively as determined by HPLC (Neff *et al.* 1994). SOS contained 1.6% tristearin as an impurity.

The solid fat content (SFC) was determined by pulsed nuclear magnetic resonance spectroscopy according to the official AOCS method (Anon 1989). A Bruker Minispec instrument was used, Toronto, ON. The temperature range studied was from 10-50°C. Drop melting points were determined according to the official AOCS method and values reported are the means of duplicate determinations (Anon 1989). The agreement between duplicates was equal to or better than the ± 1.4°C variability reported as acceptable for the method.

Heats of fusion (ΔH) were determined by differential scanning calorimetry (DSC) according to

Table I
Physical properties of structured triacylglycerols

		Solid Fat Content (SFC)@ Temp., °C[a]							Melting Point		ΔH	
											DSC[c]	Melting Point
Triglyceride	Purity, %	10	21.1	26.7	33.3	40	45	50	Drop Pt., °C[b]	DSC, °C	j/gm	j/gm
SSS	100	99.6	99.5	99.4	93.3	99.0	98.3	98.1	73.5	73.3	188.3	159.1
SOS	98.4	98.1	97.5	97.0	93.1	65.0	4.1	1.4	44.1	39.2	125.1	116.0
SLS	100	88.5	87.8	87.3	79.1	0.0	0.0	0.1	37.9	38.3	134.8	116.4
SLnS	100	87.9	86.6	79.4	38.8	0.3	0.0	0.0	36.5	38.3	134.4	129.8
EEE	100	98.8	98.6	98.1	97.6	65.0	0.0	0.0	43.5	41.6	150.7	103.0
SSL	100	88.9	88.1	87.4	86.8	60.5	0.0	0.0	42.3	31.8	138.6	133.9

[a]By pulsed NMR, AOCS method Cc 18-80
[b]AOCS method Cc 16-60
[c]AOCS method Cj 1-94

the official AOCS method (6). A TA instruments model 2910 DSC was used, New Castle, DE. Melting points by DSC were found to have a standard deviation of ±1.3% and were within the ranges reported for the methodology. Heats of fusion (ΔH) were reproducible to within ±5.1%.

3. RESULTS AND DISCUSSION

Although pulsed NMR had found widespread use to estimate solid fat in triacylglycerol oils (List *et al.* 2001), little or no data have been published for pure, individual triacylglycerols. The solid fat contents of the symmetrical triacylglycerols SOS, SLS and SlnS are given in Table I along with their drop melting points and heats of fusion. Their solid fat content over 10-50°C range shows the interesting functional properties of these triacylglycerols since, at the temperatures used to define the solid fat content of an edible oil, they show high, but sharply melting properties. Triacylglycerols which melt sharply are particularly important components of food oils since they impart a pleasant, cooling sensation in the mouth and, therefore, affect the sensory properties of spreads (Bessler and Orthoefer 1983). At temperatures of 10-33.3°C they all contain high amounts of solids (39-93%) yet are completely melted at 36-44°C. The completely saturated SSS triglyceride melts at 73.5°C, while SOS, which contains 1 double bond/molecule, melts at 44.1°C, 2 double bonds/molecule (SLS) melts at 37.9°C and 3 double bonds/molecule (SLnS) melts at 36.5°C.

Compared to the melting points of fully trisaturated triacylglycerols, including tristearin (SSS), tripalmitin (PPP), trimyristin (MMM) and trilaurin (LaLaLa), the introduction of oleic acid into the two position, forming symmetrical triacylglycerols, lowers the melting point about 30°C. For example, SSS melts at 73.5°C compared to 44.1°C for SOS, tripalmitin melts at 65.5°C compared to 35.2°C for POP, trimyristin melts at 57°C compared to 26.3°C for MOM and LaLaLa melts at 46.4°C compared to 16.5°C for LaOLa (Bailey 1950).

The heat of fusion data (ß form) for SSS, SOS and SLS are in agreement with Sato (2001) while the heat of fusion for SlnS has not been reported. Heats of fusion were also calculated from Mettler dropping point determinations as admixtures with soybean oil and the results, with the exception of SSS, showed consistent agreement with the DSC data.

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