Incorporation of medium chain fatty acids into fish oil triglycerides by chemical and enzymatic interesterification

By Maria M. C. Feltes, a L. de Oliveira Pitol, a J. F. Gomes Correia, a R. Grimaldi, b J. Mara Block c and Jorge L. Ninow, a*

a Centro Tecnológico, Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina (UFSC), Caixa Postal 476, CEP 88040-900, Florianópolis, SC, Brazil
b Faculdade de Engenharia de Alimentos, Laboratório de Oleos e Gorduras, Universidade Estadual de Campinas (UNICAMP), Campinas, SP, Brazil.
c Centro de Ciências Agrárias, Departamento de Ciência de Alimentos (UFSC), Florianópolis, SC, Brazil.
(*Corresponding author: jorge@enq.ufsc.br)

RESUMEN

Incorporación de ácidos grasos de cadena media a triglicéridos de aceite de pescado por interesterificación química y enzimática.

Triglicéridos estructurados (SL) conteniendo ácidos grasos de cadena media (MCFA) y ácidos grasos polinsaturados (PUFA) en la misma molécula de glicerol tienen ventajas nutricionales y terapéuticas. Se establece la incorporación de MCFA a los triglicéridos (TAGs) de aceite de pescado, conservando un contenido considerable de ácidos docosahexaenoico (DHA) y eicosapentaenoico (EPA). El efecto de diferentes acil donadores (éster metílico de ácido cáprico/MeC10 o triglicéridos de cadena media/TCM) y de catalizador (químico o enzimático) sobre la composición del producto de las reacciones fue estudiado. La composición de ácidos grasos de los TAGs del aceite de pescado fue modificada después de las reacciones para contener MCFA y dependió del catalizador y de los substratos. Los termogramas obtenidos por Calorimetría Diferencial de Barrido (DSC) indicaron que la interesterificación provocó alteraciones considerables de los perfiles de fusión de las muestras. Fueron producidos STs de interés en nutrición clínica conteniendo EPA y DHA, además de MCFA.


SUMMARY

Incorporation of medium chain fatty acids into fish oil triglycerides by chemical and enzymatic interesterification.

Structured triglycerides (STs) containing both medium-chain fatty acids (MCFA) and polyunsaturated fatty acids (PUFA) in the same molecule offer nutritional and therapeutic benefits. The aim of this work was to establish the incorporation of MCFA into fish oil triglycerides (TAGs), while maintaining substantial levels of docosahexaenoic and eicosapentaenoic acids. The effects of different acyl donors (capric acid methyl ester/MeC10 or medium chain triglyceride/TCM) and of the catalyst (chemical or enzymatic) on the fatty acid composition of the reaction product were studied. The fatty acid composition of the fish oil TAG was modified after interesterification to contain MCFA, and it depended on the catalyst and on the substrates. Thermograms obtained by Differential Scanning Calorimetry (DSC) showed that interesterification promoted noteworthy changes in the melting profile of the samples. STs of clinical nutrition interest containing both EPA and DHA obtained from fish oil along with MCFA were successfully produced.

KEY-WORDS: Fish oil – Interesteerification – Medium-chain fatty acid – Structured triglycerides.

1. INTRODUCTION

Medium-chain triglycerides (MCTs) containing medium-chain saturated fatty acids (MCFA, C6:0 to C12:0), show higher mobility and solubility than long-chain fatty acids (LCFA), and they are rapidly and almost completely oxidized (Bell and Bradley, 1997; Dunford, 2004; Jones et al., 2006; St-Onge and Borsarge, 2008). Therefore, MCTs are largely applied as lipid substrates in enteral and parenteral nutrition, providing energy for patients suffering from a number of disorders (Goldberg, 1994; Galante and Tenore, 2006; Nielsen et al., 2005; Mu and Porsgaard, 2005). MCT fats, however, have reduced palatability and lower digestibility than other fatty acids (Nielsen et al., 2005). Although MCFAs, mainly caprylic and capric acids, seem to be neutral with respect to their low-density lipoproteins-cholesterol (LDL-C) raising properties (Nicolosi, 1997), there are some concerns regarding the possible effects of MCFA consumption on plasma lipid concentrations (Cater et al., 1997; Kubow, 1996; Osborn and Akoh, 2002; St-Onge and Borsarge, 2005). Therefore, caprylic and capric acids are more useful in combination with long-chain polyunsaturated fatty acids (PUFAs) in formulas to provide essential fatty acids via the PUFAs (Mu and Hoy, 2000; Osborn and Akoh, 2002; Hartvigsen et al., 2003).

Commercial lipid emulsions containing a physical mixture of long-chain triglycerides (LCT) together with MCT have been used for years in
The transformation of oils mediated by lipases has been extensively studied (Macrae, 1983; Gunstone, 1999; Osborn and Akoh, 2002). Biocatalysis takes advantage of the specificity of some lipases thus allowing the production of useful molecules which cannot be obtained either chemically or naturally (Akoh, 1995; Marangoni and Rousseau, 1995; Shimada, 2006). The sn-1,3-specific lipases have been used in the range of 5 to 10% by weight of reactants to promote the incorporation, for example, of capric acid into the end positions of a TAG molecule whose central position is preferentially occupied by fatty acids of nutritional interest (Gunstone et al., 1994).

The aim of the present paper was to establish the interesterification reaction that could lead to the design of STs of clinical nutrition interest, containing MCFA along with a high n-3 EPA and DHA content. This report compares the results obtained from the fatty acid composition of the interesterified oils when using chemical (with sodium methoxide/NaOCH₃ as catalyst) and enzymatic interesterification (with a commercial immobilized sn-1,3-specific lipase). In both cases, a commercial fish oil was used as substrate and two substances were evaluated as acyl donors (capric acid methyl ester/MeC₁₀ and medium chain triglycerides/TCM).

2. MATERIALS AND METHODS

2.1. Materials

Capric acid was obtained from Sigma Chemical Co. ROPUFA n-3 “30” Food Oil was supplied by DSM Nutritional Product Ltd. Trigliceril CM® was obtained from Support Produtos Alimenticios Ltda, Brazil. Lipozyme® RMM was gift from Novozymes. This lipase is sn-1, 3-specific.

2.2. Interesterification reactions

Capric acid (C10:0) was esterified according to Klinkesorn et al. (2004). The MeC₁₀ was stored at −20 °C in a nitrogen atmosphere until use. For the reactions, the substrates were mixed as follows: ROPUFA®:MeC₁₀ (1:2, mol/mol) and ROPUFA®:Trigliceril CM® (1:1, w/w). Before the reaction, the samples were dried using a vacuum rotary evaporator at 90-95 °C for 1 h. Reactions were performed as described below.

For the chemical reaction, sodium methoxide (NaOCH₃) was prepared by heating the mixture NaOH:MeOH (1:25, w/v) to 60 °C while stirring until the complete dissolution of the reactants. The solvent was removed at 60 °C using a vacuum rotary evaporator. The catalyst was stored in a dark flask in a desiccator until use. The chemical interesterification was performed according to Díaz Gamboa and Gioielli (2003a). The reaction was carried out with magnetic stirring in a water bath. After the mixture of reactants had reached the
reaction temperature (60 °C), NaOCH₃ in fine powder was added at a mass ratio of 0.4% of reactants. After 1 h under a vacuum of 56 mmHg the reaction was stopped with the addition of 0.5 mL of an aqueous solution of 4% (m/v) citric acid (Klinkesorn et al., 2004).

For the enzymatic interesterification, the temperature was kept at 60 °C (Moura et al., 2006). The lipase Lipozyme RM IM was added at a mass ratio of 5% of reactants. The reaction took place for 6 h with magnetic stirring under a vacuum of 56 mmHg (Díaz Gamboa and Gioielli, 2003a) and it was stopped by the removal of the immobilized enzyme through centrifugation (3,000 rpm for 15 min) and filtration.

The interesterified oils were stored at −20 °C in nitrogen until analysis.

2.3. Analytical Methodology

Determination of the quality of the samples

The acid value (Method Ca 5a-40) and the peroxide value (Method Cd 8-53) of the ROPUFA n-3 '30' Food Oil® (DSM Nutritional Products Ltd) were determined according to the Official Methodology of the American Oil Chemists’ Society (AOCS, 1990). The iodine value (I.V.) of the original mixture of the oils and the interesterified oils was calculated according to the expanded formula from the American Oil Chemists’ Society Official Method Cd 1c-85 (AOCS, 1997).

Fatty acid composition

After interesterification reactions, TAG fractions were isolated from interesterified oils by thin-layer chromatography (TLC) on 20 cm silica gel 60G plates containing a fluorescent reactant (Macherey-Nagel, Germany) using the elution system hexane/ethyl ether/formic acid (80:20:2, v/v/v) (Christie, 1982).

The fatty acid composition of the samples (Trigliceril CM®, ROPUFA® fish oil and the isolated TAGs from the interesterified oils) was determined by GC after the conversion of fatty acids into their fatty acid methyl esters (Hartman and Lago, 1973). The gas chromatograph (Shimadzu Co., Japan) 17A model, equipped with a flame-ionization detector and an SP 2340 fused-silica capillary column (60 m x 0.25 mm, 0.2 µm of polyethylene glycol, Supelco). The injector and detector temperatures were 240 and 260 °C, respectively. The column temperature was held at 60 °C (80 °C); 80 °C to 240 °C (10 °C.min⁻¹); 30 min at −40 °C; −40 °C to 80 °C (5 °C.min⁻¹). The following parameters were obtained from thermograms: melting enthalpy (J.g⁻¹), initial and final melting temperatures (°C), onset melting temperature (°C), and maximum peaks (°C).

3. RESULTS AND DISCUSSION

The acid and the peroxide values of the ROPUFA® fish oil were 0.44% of oleic acid and 1.46 meq O₂.kg⁻¹, respectively. These results agree with supplier specifications and match international regulations whose criteria of quality for refined oil include a peroxide value lower than 10 meq O₂.kg⁻¹ (FAO-WHO, 1981, revision 1999) or 5 meq O₂.kg⁻¹ in the case of oil extracted from herring (FDA, 1995, revision 2003).

The fatty acid composition of the samples as determined by GC is shown in Table 1. The total n-3 fatty acid content in the original ROPUFA® fish oil was 31.92 %, with a predominance of EPA and DHA, and no MCFA was identified in this sample. Such a composition is a characteristic feature of marine oils (Pigott and Tucker, 1990; Aro et al., 2000). Capric and caprylic acids were responsible for more than 98% of the Trigliceril CM® fatty acid composition.

The choice of the reaction conditions during synthesis of the STs was based on a previous study concerning the chemical and the enzymatic synthesis of STs containing MCFAs from palm kernel fat and n-3 PUFA from fish oil (Díaz Gamboa and Gioielli, 2003a). The conditions applied by these authors for the enzymatic reaction are in agreement with other results found in the literature for similar substrates (Jennings and Akoh, 1999; Jennings and Akoh, 2001). In the latter work, these authors have observed that a high incorporation of capric acid into fish oil was achieved at an enzyme load of 5 % (by mass of substrates) for the solvent-free reaction using the lipase Lipozyme® RM IM. The enzymatic reaction temperature was established in accordance with another work involving the reaction between n-3 PUFA ethyl esters and MCT (Moura et al., 2006). In the present study, the substrates were mixed in a ratio that allowed the inclusion of the capric acid
confirms the exchange of acyl groups among substrates during interesterification (Reyes and Hill, 1994; Marangoni and Rousseau, 1995; Rousseau and Marangoni, 2002; Xu, 2004).

In this study, the reaction conditions favored the occurrence of chemical interesterification: the concentration of the catalyst (0.4% by weight of reactants) was greater than concentrations commonly used (0.1-0.2% by weight) (Marangoni and Rousseau, 1995), while the media was extremely apolar, and there was also no solvent. Despite this, MCFA incorporation was greater for the enzymatic reaction than for the chemical reaction regardless of the substrate. Furthermore, the EPA and DHA content of the enzymatically interesterified oils remained close to that of the

### Table 1

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>ROPUFA&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Triglyceril CM&lt;sup&gt;b&lt;/sup&gt;</th>
<th>After CI&lt;sup&gt;c&lt;/sup&gt;</th>
<th>After EI&lt;sup&gt;c&lt;/sup&gt;</th>
<th>After CI&lt;sup&gt;d&lt;/sup&gt;</th>
<th>After EI&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6:0</td>
<td>–</td>
<td>1.23</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C8:0 (Caprylic)</td>
<td>–</td>
<td>63.13</td>
<td>14.04</td>
<td>18.68</td>
<td>0.10</td>
<td>0.70</td>
</tr>
<tr>
<td>C10:0 (Capric)</td>
<td>–</td>
<td>34.99</td>
<td>10.35</td>
<td>11.22</td>
<td>4.44</td>
<td>9.04</td>
</tr>
<tr>
<td>C12:0</td>
<td>–</td>
<td>0.81</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C14:0</td>
<td>6.49</td>
<td>–</td>
<td>5.56</td>
<td>4.75</td>
<td>6.22</td>
<td>6.05</td>
</tr>
<tr>
<td>C14:1</td>
<td>0.30</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C15:0</td>
<td>1.05</td>
<td>–</td>
<td>–</td>
<td>0.68</td>
<td>–</td>
<td>0.66</td>
</tr>
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<td>C16:0</td>
<td>19.58</td>
<td>–</td>
<td>19.42</td>
<td>15.50</td>
<td>18.98</td>
<td>17.44</td>
</tr>
<tr>
<td>C16:1</td>
<td>5.97</td>
<td>–</td>
<td>4.39</td>
<td>3.59</td>
<td>6.75</td>
<td>6.52</td>
</tr>
<tr>
<td>C17:0</td>
<td>0.72</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.55</td>
<td>0.61</td>
</tr>
<tr>
<td>C17:1</td>
<td>0.54</td>
<td>–</td>
<td>–</td>
<td>0.10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C18:0</td>
<td>3.65</td>
<td>–</td>
<td>3.42</td>
<td>2.80</td>
<td>3.66</td>
<td>3.26</td>
</tr>
<tr>
<td>C18:1n9t</td>
<td>2.36</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C18:1n9c</td>
<td>17.38</td>
<td>–</td>
<td>19.38</td>
<td>15.83</td>
<td>20.01</td>
<td>18.03</td>
</tr>
<tr>
<td>C18:2n6c</td>
<td>2.99</td>
<td>–</td>
<td>2.51</td>
<td>2.15</td>
<td>3.39</td>
<td>0.12</td>
</tr>
<tr>
<td>C20:0</td>
<td>0.62</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>0.40</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>0.78</td>
<td>0.71</td>
</tr>
<tr>
<td>C18:4n3</td>
<td>1.94</td>
<td>–</td>
<td>–</td>
<td>1.86</td>
<td>1.95</td>
<td>–</td>
</tr>
<tr>
<td>C20:1</td>
<td>1.10</td>
<td>–</td>
<td>–</td>
<td>1.78</td>
<td>2.11</td>
<td>–</td>
</tr>
<tr>
<td>C18:3n3</td>
<td>1.26</td>
<td>–</td>
<td>–</td>
<td>0.45</td>
<td>0.39</td>
<td>–</td>
</tr>
<tr>
<td>C20:2</td>
<td>0.39</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.27</td>
<td>0.18</td>
</tr>
<tr>
<td>C22:0</td>
<td>0.27</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>C20:3n6</td>
<td>1.51</td>
<td>–</td>
<td>–</td>
<td>0.78</td>
<td>0.71</td>
<td>–</td>
</tr>
<tr>
<td>C20:3n3</td>
<td>0.24</td>
<td>–</td>
<td>–</td>
<td>0.78</td>
<td>0.71</td>
<td>–</td>
</tr>
<tr>
<td>C22:2</td>
<td>0.97</td>
<td>–</td>
<td>–</td>
<td>0.78</td>
<td>0.71</td>
<td>–</td>
</tr>
<tr>
<td>C20:4n6</td>
<td>0.45</td>
<td>–</td>
<td>–</td>
<td>0.78</td>
<td>0.71</td>
<td>–</td>
</tr>
<tr>
<td>C20:5n3 (EPA)</td>
<td>11.17</td>
<td>–</td>
<td>7.51</td>
<td>12.33</td>
<td>11.06</td>
<td>11.85</td>
</tr>
<tr>
<td>C22:5n3</td>
<td>1.07</td>
<td>–</td>
<td>–</td>
<td>0.68</td>
<td>0.53</td>
<td>–</td>
</tr>
<tr>
<td>C22:6n3 (DHA)</td>
<td>19.68</td>
<td>–</td>
<td>13.42</td>
<td>13.17</td>
<td>15.19</td>
<td>17.52</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

| Saturated   | 32.38           | 100.00          | 52.79          | 52.95          | 36.54          | 38.34          |
| Monounsaturated | 27.65       | –               | 23.77          | 19.42          | 28.62          | 26.50          |
| Polyunsaturated | 39.96       | –               | 23.44          | 27.65          | 34.84          | 35.18          |
| Total       | 100.00          | 100.00          | 100.00         | 100.00         | 100.00         | 100.00         |

| EPA:DHA     | 0.57            | –               | 0.56           | 0.94           | 0.73           | 0.68           |
| n3:n6       | 8.34            | –               | 8.34           | 11.86          | 6.02           | 15.81          |
| Iodine value| 187             | –               | 120            | 134            | 157            | 166            |

<sup>a</sup> After CI = After chemical interesterification.
<sup>b</sup> After EI = After enzymatic interesterification.

into two positions of the ROPUFA<sup>a</sup> triglycerides when the MeC<sub>10</sub> was applied as substrate (1:2, mol:mol, ROPUFA<sup>a</sup>:MeC<sub>10</sub>), as previously stated by Jennings and Akoh (1999) for the esterification of capric acid to fish oil TAG by means of an enzymatic reaction with the lipase Lipozyme<sup>b</sup> RM IM. In the case of the interesterification between the ROPUFA<sup>a</sup> and the Triglyceril CM<sup>c</sup>, the ratio 1:1 (w/w) was chosen because it is usually applied for the physical mixture of LCT and MCT applied in enteral and parenteral nutrition (Hasselmann and Kummerlen, 1998).

After both the chemical and the enzymatic reaction between the fish oil and the acyl donor (Triglyceril CM<sup>c</sup> or MeC<sub>10</sub>), MCFA were detected in the TAGs of the interesterified oils. This composition confirms the exchange of acyl groups among substrates during interesterification (Reyes and Hill, 1994; Marangoni and Rousseau, 1995; Rousseau and Marangoni, 2002; Xu, 2004).

In this study, the reaction conditions favored the occurrence of chemical interesterification: the concentration of the catalyst (0.4% by weight of reactants) was greater than concentrations commonly used (0.1-0.2% by weight) (Marangoni and Rousseau, 1995), while the media was extremely apolar, and there was also no solvent. Despite this, MCFA incorporation was greater for the enzymatic reaction than for the chemical reaction regardless of the substrate. Furthermore, the EPA and DHA content of the enzymatically interesterified oils remained close to that of the

GRASAS Y ACEITES, 60 (2), ABRIL-JUNIO, 168-176, 2009, issn: 0017-3495, DOI: 10.3989/gya.074708 171
original values. These results agree with others which show that lipases discriminate strongly between MCFA and LCFA in favor of MCFA (Akoh, 1995; Kubow, 1996; Bell and Bradley, 1997; Osborn and Akoh, 2002).

The use of MeC10 as acyl donor led to a higher content of EPA and DHA after the reaction. The total EPA and DHA content in the interesterified Trigliceril CM® and ROPUFA® oils was 20.93% and 25.50% for the chemical and the enzymatic reactions, respectively. The total EPA and DHA content in the MeC10 and the ROPUFA® oil was 26.25% and 29.37% after chemical and enzymatic interesterification, respectively. The success of the use of mcty esters as substrates for interesterification reactions has been previously demonstrated in another study whose objective was the enrichment of tuna oil with EPA and DHA by chemical transesterification (Klinkesorn et al., 2004).

A previous study (Moura et al., 2006) also reported the efficiency of the incorporation of long-chain esters (of the ethyl type), obtained from fish oil, into MCT, at a molar ratio of 1:2.5, respectively, chain esters (of the ethyl type), obtained from fish oil reported the efficiency of the incorporation of long-

ratio of 2:1, respectively, was performed over 24 h at 60 °C with stirring and under vacuum, the highest yield of binary mixtures between palm kernel oil (rich in MCFA) and another fish oil (menhaden fish oil from National Marine Fisheries Service, USA). TAGs were produced with an average of 28.8 mol% of C10:0, predominantly located in the central position of TAGs, thus obtaining a specific ST with nutritional interest.

In another study, the incorporation of C10:0 into fish oil TAGs (Prinova Biocare, Noruega), at a molar ratio of 2:1, respectively, was performed over 24 h at 55 °C and 200 rpm by using an immobilized sn-1,3-specific lipase (10 % by weight of reactants). The authors obtained a final product with an average of 43 mol% of C10:0 in TAGs for the reaction in the presence of hexane, and 31.8 mol% for the solvent-free reaction. It was found that EPA and DHA were predominantly located in the central position of TAGs, thus confirming the ST synthesis, even with some acyl migration (Jennings and Akoh, 1999).

The same researchers outlined the same reaction conditions for the enzymatic modification of another fish oil (methingen fish oil from National Marine Fisheries Service, USA). TAGs were produced with an average of 28.8 mol% of C10:0, predominantly located in the end positions (Jennings and Akoh, 2001).

Others have described the possibility of the synthesis of STs containing MCFAs, EPA and DHA by both chemical and enzymatic interesterification of binary mixtures between palm kernel oil (rich in lauric acid) and fish oil. The chemical reaction was performed over 1 h at 60 °C with stirring and under reduced pressure, with sodium methoxide as catalyst (0.4 % by weight of reactants). A final product was obtained with plastic behavior and containing G = 5.0 to 23.4% of n-3 PUFAs (Díaz Gamboa and Gioielli, 2003a). The enzymatic interesterification was carried out over 6 h at 65 °C in a nitrogen atmosphere by using a commercial sn-1,3-specific lipase (5% by weight of reactants) (Díaz Gamboa and Gioielli, 2003b).
Capric acid has a melting point greater than that of its methyl ester, thus leading to TAGs with a greater melting point. Further, capric acid has a melting point greater than that of caprylic acid, which in turn is the main fatty acid in the Trigliceril CM® (Bailey, 1979; ISEO, 2006). Hence, the thermograms shifted a few degrees higher when using MeC10 as acyl donor.

Information on the characteristic temperatures of the samples was obtained from thermograms and the values are shown in Table 2. The very low or negative melting temperatures obtained for the oils can be attributed to the presence of unsaturated fatty acids in all samples, provided from the fish oil. This behavior has been already observed for salmon oil (Sathivel, 2005) and is a special feature of fish oils. According to another ST containing MCFAs and n-3 PUFAs mentioned in the United States Patent 6.608.223 (Rao et al., 2003), the STs obtained herein as a result of interesterification reactions alike, with just one peak of similar shape, suggesting little difference between TAGs obtained by chemical and enzymatic interesterification.

The DSC thermograms of the fish oils interesterified with the MeC10 (Figure 2) exhibited a broad melting range, with two distinct peaks for the product of the chemical reaction, probably because of a random distribution of fatty acids in TAGs. The higher complexity of the thermograms shown in Figure 2 suggests a higher complexity of the STs obtained by the interesterification between the fish oil and the MeC10. This result could also be associated with the formation of TAGs without intersolubilization, which is consistent with other studies involving TAG modification (Rousseau et al., 1996; Nassu and Gonçalves, 1999).

Capric acid has a melting point greater than that of caprylic acid, which in turn is the main fatty acid in the Trigliceril CM® (Bailey, 1979; ISEO, 2006). Hence, the thermograms shifted a few degrees higher when using MeC10 as acyl donor.

Information on the characteristic temperatures of the samples was obtained from thermograms and the values are shown in Table 2. The very low or negative melting temperatures obtained for the oils can be attributed to the presence of unsaturated fatty acids in all samples, provided from the fish oil. This behavior has been already observed for salmon oil (Sathivel, 2005) and is a special feature of fish oils. According to another ST containing MCFAs and n-3 PUFAs mentioned in the United States Patent 6.608.223 (Rao et al., 2003), the STs obtained herein as a result of interesterification reactions alike, with just one peak of similar shape, suggesting little difference between TAGs obtained by chemical and enzymatic interesterification.

The DSC thermograms of the fish oils interesterified with the MeC10 (Figure 2) exhibited a broad melting range, with two distinct peaks for the product of the chemical reaction, probably because of a random distribution of fatty acids in TAGs. The higher complexity of the thermograms shown in Figure 2 suggests a higher complexity of the STs obtained by the interesterification between the fish oil and the MeC10. This result could also be associated with the formation of TAGs without intersolubilization, which is consistent with other studies involving TAG modification (Rousseau et al., 1996; Nassu and Gonçalves, 1999).
important role in the establishment of the fatty acid composition of the interesterified oils. We described the incorporation of MCFA into fish oil TAGs with the maintenance of a high EPA and DHA content mainly when using MeC10 as acyl donor in the enzymatic interesterification. The STs herein obtained have relatively high amounts of PUFAs accompanying the MCFAs. The STs thus obtained have potential application in clinical nutrition as an energy-yielding substrate rich in essential fatty acids, particularly beneficial for patients with malabsorption syndromes.

ACKNOWLEDGMENTS

The authors thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for providing a Master’s Fellowship, Novozymes, DSM Nutritional Products Ltd and Support Produtos Alimentícios Ltda. for donations, Prof. Francisco C. Deschamps (Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina S.A., Brazil) for his assistance in GC analysis and Prof. Luiz A. Gioielli (Universidade Estadual de São Paulo, Brazil) for his suggestions.

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Moura JMLN de, Gonçalves LAG, Grimaldi R, Soares M da S, Ribeiro APB. 2006. Otimização das condições de produção de ésteres etílicos a partir de óleo de...

Recibido: 3/7/08
Aceptado: 28/10/08