STUDIES ON THE CHEMICAL PROPERTIES OF MEDIUM CHAIN TRIGLYCERIDES AND ACETOGLYCERIDES

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INTRODUCTION

Medium chain triglycerides (MCT) differ from normal triglycerides in their physiological behaviour and therefore they have therapeutical importance. They are used for the treatment of diseases of the digestive tract, e.g. syndromes of maldigestion and malabsorption [2, 3, 5, 7]. Furthermore MCT influence the levels of blood lipids, they especially lower the cholesterol level [11, 12].

Medium chain fatty acids are hardly laid down in the fat depots. Feeding only MCT as fat source is also energy consuming, because the long chain fatty acids, which can be accumulated in the fat depots, are to be synthetized by metabolic reactions. Therefore the energy retention is reduced and it is possible to achieve body weight reduction by MCT diet. So, rats fed with MCT diet have a 25% higher energy demand for the maintenance of constant body weight than rats fed with lard diet [8].

MCT don't occur in natural fats. Usually they are synthetized by catalytic esterification of glycerol with medium chain fatty acids, obtained by hydrolysis of coconut or palm kernel oil and fractionation of the fatty acids [2, 13]. Thus the production of MCT is connected with high demands for technical equipment and with expensive import of the raw materials.

Therefore we were looking for other fats to replace MCT. We suppose that acetoglycerides also can influence serum lipids and energy retention, because they contain fatty acids with low molecular weight which cannot be laid down in the fat depot. Long chain fatty acids can be synthetized only from the aceto groups via energy consuming reac-

tions. Numerous reports and papers are concerned with biochemistry and therapeutical use of MCT, but in the literature are only a few informations about their chemistry, especially about their chemical stability. Therefore we have tested the storage behaviour of MCT and acetoglycerides.

MATERIALS AND METHODS

MCT have been synthetized by esterification of glycerol with pure capric acid or a mixture of 13% caprylic and 87% capric acid using phosphoric acid and other catalysts at various temperatures. The esterification product has been purified by a alumina column.

Acetoglycerides have been produced by interesterification of sunflower oil with triacetin 1 : 2 (mole ratio 1 : 12) at 70°C using 0.5% sodium methylate as catalyst. After a reaction time of 1 hour the exceeding triacetin is removed by distillation. The reaction product is washed with water. In order to test the storage stability, we have used the pure fats and fats as components of margarine blends, consisting of 79%, 20% water, and 1% emulsifying agent. Furthermore we used the fats as components of formula mixtures, consisting of 21% fat, 18.3% casein, 25% lactose, and 35,8% starch.

We carried out the storage experiments at room temperature. In order to evaluate the chemical stability we determined the FFA content [4, 9], the peroxide number [6], and the carbonyl content [10].

RESULTS

ESTERIFICATION REACTION

The first item is directed to find optimal conditions for esterification medium chain faty acids with glycerol. The results are summarized in Table. As results from literature, stannic chloride is frequently used for this purpose. In our trials we need esterification time of 10 hours, but we get brown coloured products with a high carbonyl content. The catalysts zinc chloride and zinc powder are not so useful, because the esterification is very time consuming and the products are brown and have a high carbonyl content, too. We could get the best results with phosporic acid. At a temperature of 180°C, the reaction is rather fast and, using amounts of 0.5% phosphoric acid the reaction products are bright and have a low carbonyl content.

Table

Effect of catalyst and temperature on speed of esterification and quality of esterified tricaprin

Catalyst	Temperature [°C]	Esterification time [hrs] *		Esterification product		
		T_1	T_2	colour	light absorption**	carbonyl content***
0.15% $SnCl_2.2\,H_2O$	160	10	1	yellow-brown	43.4	53.7
0.12% $ZnCl_2$	160	18	2	dark-brown	120.0	65.6
0.2% Zn (powder)	160	16	1.5	brown	43.3	36.1
0.15% $SnCl_2.2\,H_2O$ 0.15% citric acid 0.01% propyl gallate	160	12	1.5	yellow-brown	11.8	31.0
0.2% H_3PO_4	160	16	2	yellowish	6.2	4.8
0.2% H_3PO_4	180	8	1	light yellow	3.7	29.6
0.5% H_3PO_4	180	8	1.5	light yellow	1.4	4.8
0.2% H_3PO_4 0.15% citric acid 0.01% propyl gallate	180	9	2	yellowish	1.9	5.0

* T_1 — total esterification time.
T_2 — time for esterification of half the amount of acid.

** $E^{1\%}_{1\ cm\ 450\ nm} \times 10^3$

*** [mg heptanal/g substrate].

CHEMICAL STABILITY OF MCT

The first experiments are concerned with storage stability of chromatographically purified tricaprin. The changes of FFA content can be seen in Figure 1. According to this the FFA content of pure tricaprin and tricaprin as a component of a formula mixture does almost not increase. In contrast to this a tricaprin margarine blend shows a quick increase of FFA content. The determination of peroxide number and carbonyl content points out that changes during storage seem not to happen in a remarkable degree. Further experiments were carried out in order to find influences on the hydrolysis rate of MCT in margarine blends. We

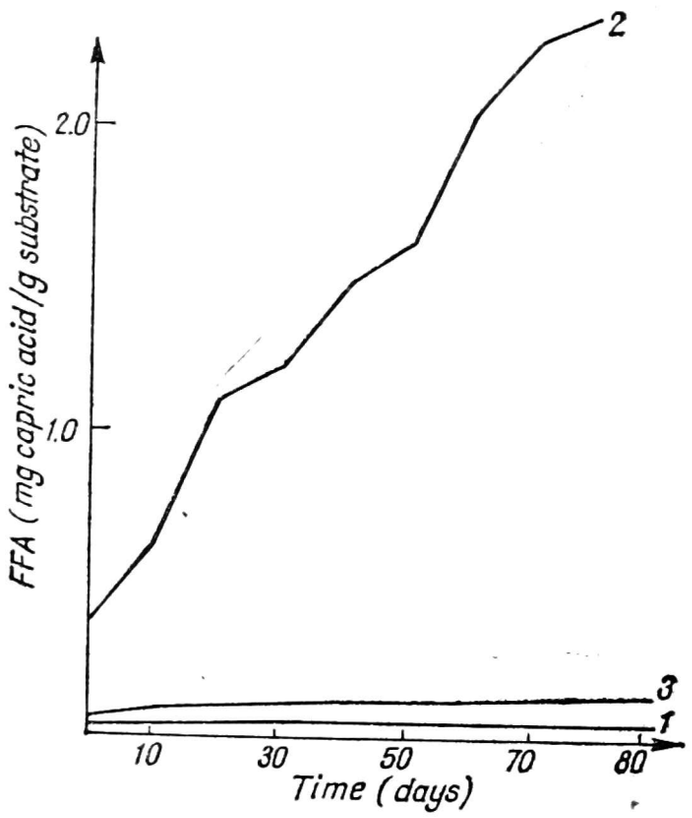

Fig. 1. Chemical stability of tricaprin, expressed by changes of FFA content: *1* — tricaprin, *2* — tricaprin in margarine blend, *3* — tricaprin in formula mixture

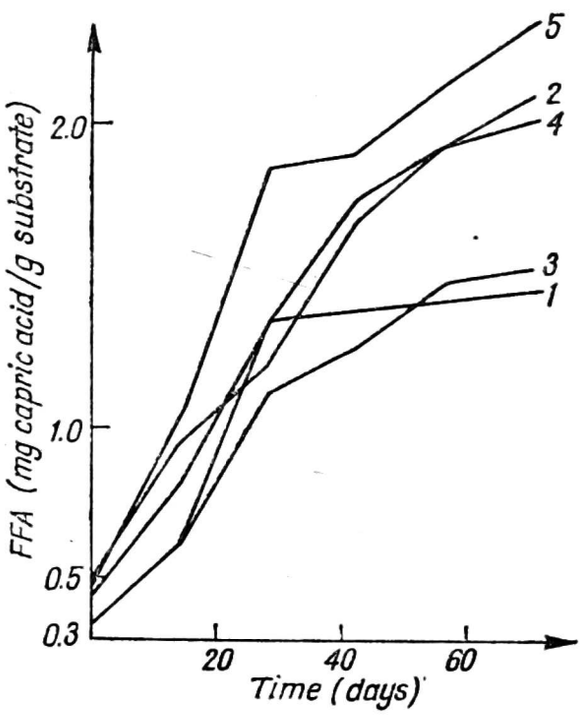

Fig. 2. Influence of water binding agents on chemical stability of MCT in margarine blends, expressed by changes of FFA content: *1* — MCT, *2* — 5% starch hydrolyse products, 5% pectin, 4.5% microcristalline cellulose, *5* — sunflower oil (comparison)

used triglycerides containing caprylic and capric acid. The effect of some water binding agents e. g. microcristalline cellulose, carboxymethyl starch, starch hydrolysis products, pectin, gelatine, and others, in amounts of 1 or 5% has been examined.

Figure 2 shows the influence of starch hydrolysis products, pectin and microcristalline cellulose on the changes of FFA content of MCT margarine during storage, additionally the FFA changes of MCT mar-

garine without additions and of a margarine blend, prepared from sunflower oil are presented. The alterations of the FFA content of all margarine blends are nearly of the same extent. Starch hydrolysis products, pectin, and microcristalline cellulose don't inhibit the hydrolysis of MCT, the same fact has been found for the other water binding agents. The changes of carbonyl content and peroxide value of these margarine samples have been investigated too, but they show only a very slow increase except sunflower oil.

CHEMICAL STABILITY OF ACETOGLYCERIDES

The chemical stability of acetoglycerides has been tested with pure acetoglycerides and with acetoglycerides as components of margarine blend and formula mixture, respectively. The storage behaviour is compared with that of sunflower oil, from which the acetoglycerides are prepared.

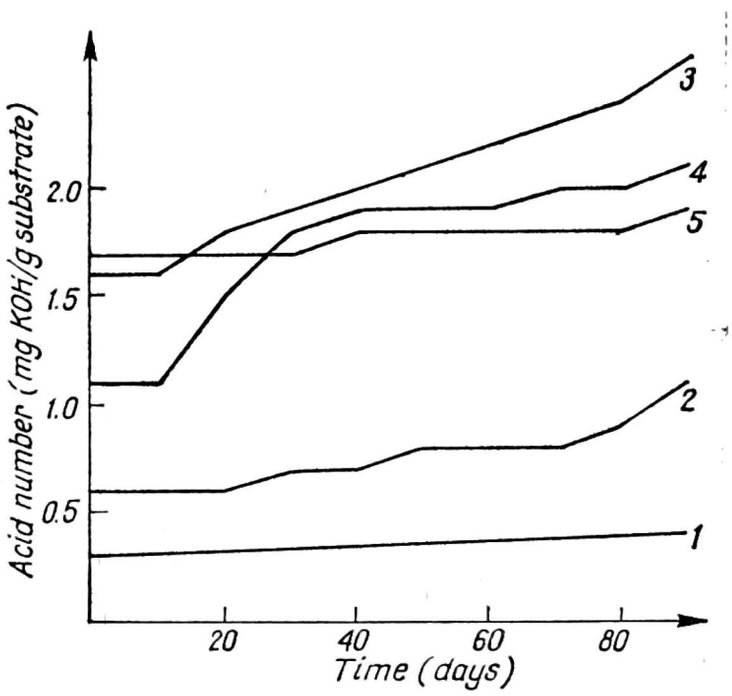

Fig. 3. Chemical stability of acetoglycerides, expressed by changes of acid number: *1* — sunflower i oil (comparison), *2* — acetoglycerides, 3 — acetoglycerides in margarine blend, *4* — acetoglycerides + 0.01% propyl gallate + 0.1% citric acid, *5* — acetoglycerides in formula mixture

Figure 3 shows the changes of FFA content during storage. The acid number of the sunflower oil shows the lowest increase, but the increase of FFA content of acetoglycerides per se and in the formula mixture is slowly too. The acetoglycerides show the highest hydrolysis rate in the margarine blend.

The changes of the peroxide number during the storage are summarized in Fig. 4. The pure acetoglycerides show the highest rate of peroxide formation. Acetoglycerides in the margarine blend and other mixtures which are protected against autoxidation by the antioxidant propyl gallate, show, according to the expections, a low increase of peroxide number.

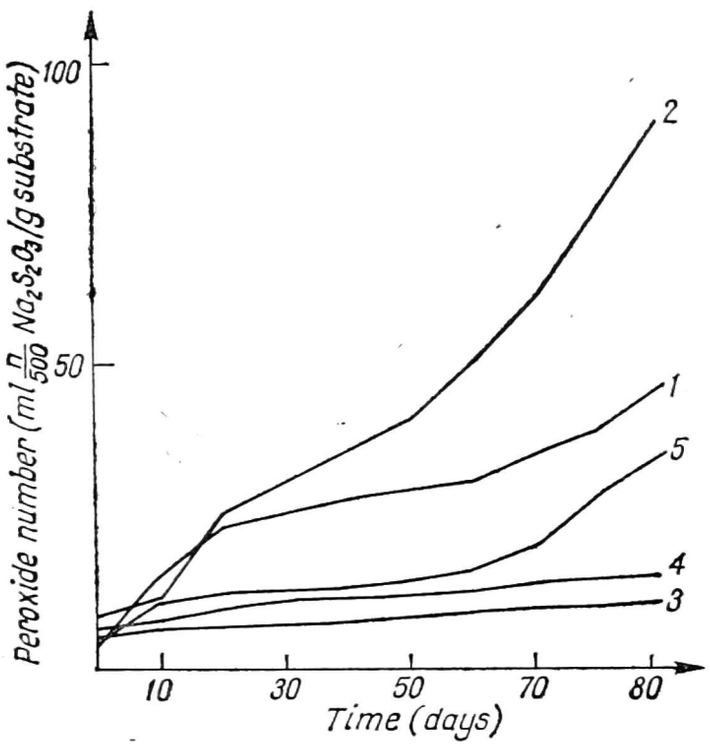

Fig. 4. Chemical stability of acetoglycerides, expressed by changes of peroxide number: *1* — sunflower oil (comparision), *2* — acetoglycerides, *3* — acetoglycerides in margarine blend, *4* — acetoglycerides + 0.01% propyl gallate + 0.1% citric acid, *5* — acetoglycerides in formuła mixture

DISCUSSION

Our experiments show, that the chemical stability of MCT is limited by hydrolytic reactions, while oxidation reactions are only of small importance. The fatty acids of snuflower oil have, according to our tests, nearly the same hydrolysis rate, but the free long chain fatty acids are, organoleptically seen, not so bad as free caprylic or capric acid.

In organoleptic experiments we have tested the sensitivity of several test persons against free capric acid in fat emulsions. The detection limit lies between 0.1 and 0.5 mg capric acid per gram emulsion. This means that the margarine blends have only a very short storage stability. Our trails for lowering the hydrolytic reactions by addition of water binding agents were not successful.

The chemical stability of acetoglycerides depends essentially on the composition of the fat, from which the acetoglycerides are prepared. We prefer a vegetable oil rich in linoleic acid, e. g. sunflower is not high. In our trials the peroxide number of acetoglycerides increases faster than that of sunflower oil, because the acetoglycerides have undergone a thermal treatment during their preparation or by the influence of free acetic acid. The oxidation reactions are inhibited by addition of antioxidants and in margarine blends. The water droplets are probably forming a shield around the fat particles and so they protect the fat against oxygen. On the other hand, the presence of water causes hydrolytic splitting of acetoglycerides. In organoleptic tests we stated an sensitivity limit of 0.5 mg free acetic acid in fat emulsions. We think, that

the danger of hydrolysis is a serious reason against the development and production of water containing foods, containing MCT and acetoglycerides in their fat constituents. Such fats should therefore preferentially by used as pure fats for preparing meals or in dry formula mixtures.

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STUDIA NAD CHEMICZNYMI WŁASNOŚCIAMI ŚREDNIOŁAŃCUCHOWYCH TRÓJGLICERYDÓW I ACETOGLICERYDÓW

Streszczenie

Średniołańcuchowe trójglicerydy są syntetyzowane przez estryfikację glicerolu kwasami tłuszczowymi o średniej długości łańcucha. Autorzy badali wpływ temperatury i różnych katalizatorów na szybkość estryfikacji.

Acetoglicerydy otrzymywano przez transestryfikację oleju słonecznikowego trójacetyną, używając metanolanu sodowego jako katalizatora. Chemiczna stabilność średniołańcuchowych trójglicerydów i acetoglicerydów jest określana przez czas magazynowania prób, liczbę nadtlenkową i kwasową oraz zawartość związków karbonylowych.

Testy dotyczyły czystych tłuszczów, tłuszczów jako części zestawów margarynowych (osnów margarynowych) i wzorcowych diet. Chemiczna stabilność średniołańcuchowych trójglicerydów jest głównie limitowana przez reakcje hydrolityczne. Badany był wpływ związków wiążących wodę na stabilność. Zachowanie się acetoglicerydów podczas przechowywania porównano z zachowaniem się oleju słonecznikowego. Wyniki wskazują, że kwas octowy zawarty w trójglicerydach ma tylko niewielki wpływ na stabilność.

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ИССЛЕДЕВАНИЯ ХИМИЧЕСКИХ СВОЙСТВ ТРИГЛИЦЕРИДОВ СО СРЕДНИМИ ДЛИНАМИ ИЕПЕЙ И АЦЕТОГЛИЦЕРИДОВ

Р е з ю м е

Триглицериды со средними длинами иепей синтизируются путем этрификации глицерола жирными кислотами со средней длиной цепи. Авторы усследовали влияние температуры и разных катализаторов на скорость этерификации.

Ацетоглицериды получали путем трансэтерификации подсолнечного масла триацетилом, с использованием натриового метанола в качестве катализатора. Химическую стабильность маргарина и ацетоглицеридов определяет время хранения образцов, пероксидоное и кислотное число и содержание карбонильных соединений.

Тесты охватывали чистые жиры, жиры как части маргаринных составов (основ) и стандартные диэты. Химическую стабильность маргарина ограничивают гидролитические реакции. Исследовали влияние связывающих воды соединений на стабильность. Поведение ацетоглицеридов во время хранения сравнивали с поведением подсолнечникового масла. Результаты показали, что содержание в глицеридах уксусной кислоты лишь незначительно влияет на стабильность.