ISSN 2664-9969

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UDC 664.3
DOI: 10.15587/2706-5448.2020.218645

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ANALYSIS OF THE ETHYL STEARATE PROPERTIES AS A NEW ALTERNATIVE TO COCOA BUTTER

The object of research is the product of modification of fats, in particular derivatives of fatty acids and monohydric alcohols, namely ethyl stearate. One of the biggest challenges for the confectionery industry is the use of modified fats that fully meet food safety requirements. Existing modified fats, used in confectionery, mainly contain saturated fatty acids with carbon atoms of 16 or less, identified by the World Health Organization (WHO) as harmful to the human body. Without the presence of a significant amount of trans fatty acids, it is difficult to obtain inexpensive modified fats that have high hardness at a low melting point. The reduction of trans fatty acid isomers in modified fats is a worldwide problem. In addition, the presence of glycerol in the composition of trihydric alcohol fats can promote the formation of glycidol esters. In turn, glycidol esters are known to contribute to the development of cancer. It is practically impossible to obtain triacylglycerols, which contain only stearic acid among the saturated fatty acids. This is a significant obstacle to the formation of a rational fatty acid composition in terms of the content of saturated acids.

It is proposed to solve certain problems by means of a new technology for modifying fats, namely by replacing in the composition of fats – acylglycerol of the alkyl group. As an alternative to cocoa butter in confectionery products, according to the author's data, stearic acid ethyl ester can be used. A complex of studies has determined that ethyl stearate, by its physical and chemical properties, namely: melting point, mass fraction of solid ethers and solubility in acylglycerols in any ratio, is a full-fledged alternative to cocoa butter.

The use of new modified fats, in particular ethyl stearate in the composition of confectionery, will allow to exclude saturated fatty acids from the diet; according to WHO, they contribute to an increase in low density lipoproteins in human blood.

Keywords: *fat and oil industry, modified fats, ethyl esters of fatty acids, stearic acid, confectionery industry.*

Received date: 20.08.2020
Accepted date: 23.09.2020
Published date: 31.12.2020

1. Introduction

A promising direction in the fat and oil industry is the production of modified fats by changing the composition of the alkyl group, that is, the conversion of fatty acids into ethers of monohydric alcohols, in particular ethyl alcohol. In this way, it is easy to obtain modified fats with high hardness and low melting point without trans-isomers, as well as selectively regulate their fatty acid composition [1]. Full or partial replacement of fats in ethyl esters of fatty acids will allow creating compositions with a narrow range of melting points, hardness and other structural, mechanical and physicochemical properties, which is extremely important for the confectionery industry.

Difficulties in the creation of fats without trans fatty acid isomers (TFAI) lead to a decrease in demand for margarine products from consumer industries [2]. In many countries, regulation has been introduced for the TFAI content in finished products. For example, in Ukraine, at the legislative level, this indicator is limited in spreads (DSTU 4445:2005), sandwich margarines (DSTU 4465:2005) and minarines (DSTU 4564:2006) to 8 %. For other products regulating the TFAI content is absent [3]. The production of margarine is partially supported by modified fats with a minimum amount of trans isomers (2 g per 100 g of product), but such technologies have been introduced at some enterprises (for example, Kyiv Margarine Plant, Ukraine). As for special-purpose fats, in particular, confectionery fats, their production is provided, in the overwhelming majority, through the processing of palm and palm kernel oils (these are such enterprises as KAPRO OIL, Schedro, Delta Wilmar Ukraine). The requirements for such fats are regulated by the DSTU 4335:2004 standard.

Confectionery fats also include cocoa butter equivalents, improvers, substitutes and surrogates, the requirements for which are specified in the DSTU 5005:2014 standard. Such alternative fats differ in production technologies and raw materials from which they are obtained. Fractionation in combination with traditional methods for modifying oils and fats such as hydrogenation and transesterification is the main technology for producing alternative cocoa butter fats. The chemical composition of tempered and untempered fats, alternative to cocoa butter, is slightly different. The former fully reproduce the acylglycerol composition of natural cocoa butter and have no more than 2 % TFAI. For their manufacture, tropical oils are used (shea, sat, mango, illipe, palm and others). The latter are divided into 2 types: lauric and non-lauric. Modified lauric fats are derived from palm kernel and coconut oils, which have a high lauric acid content. The production of non-lauric fats consists in the processing of oils rich in palmitic, stearic and oleic fatty acids (soybean, cottonseed, palm, sunflower, illipe, kokum, shea, etc.). Such oils are subjected to hydrogenation and/or fractionation processes, as a result of which 1-palmito-2,3-dielaidinoylglycerol and 1-palmito-2-yelaidin-3-stearoylglycerol appear in their composition [4].

In the production of chocolate, only natural cocoa butter is used as a fat base, and in the manufacture of chocolate products, in addition to cocoa butter or instead of it – fats, alternative to it (equivalents, substitutes).

The high price of natural cocoa butter and the constant increase in the range of chocolate products stimulate the development of the production of fats alternative to cocoa butter. Such fats are characterized by high hardness and low melting points and are difficult to reproduce without the use of hydrogenated fats and tropical oils.

The use of ethyl stearate in the composition of confectionery products will allow excluding trans fatty acid isomers from the diet, as well as saturated acids of the C16 series and less. Such fatty acids, as defined by the World Health Organization (WHO), are harmful to the human body and contribute to the development of heart disease. So, the relevance of research is confirmed by the need to improve the technology for the production of food products for the safety of their consumption by humans. Thus, *the object of research* is the product of modification of fats, in particular derivatives of fatty acids and monohydric alcohols, namely, ethyl stearate. And *the aim of research* is to analyze the physicochemical properties of ethyl stearate in the context of the proposal to include ethyl stearate DSTU 5005 as a new alternative to cocoa butter.

2. Methods of research

It is known that the current technologies do not allow creating alternatives to cocoa butter, without the use of hydrogenated fats and tropical oils. Fats modified by hydrogenation contain TFAI, the consumption of which for humans, according to WHO recommendations, should be reduced to a minimum (no more than 1 % of the daily caloric intake). This is evidenced by the introduction of restrictions on their content in food, as noted above. Tropical oils and products of their processing, massively cover the need for solid low-melting fats, have no less threat to human health than hydrogenated fats.

First, the high content of saturated fatty acids, mainly palmitic, myristic and lauric, which, according to WHO, affect the increase in low density lipoprotein (LDL) in human blood plasma, and therefore lead to the development of cardiovascular diseases (CVD). The fatty acid composition of tropical oils, massively altered and consumed, are given in Table 1 [3].

Table 1

Fatty acid composition of tropical oils

Oil name	Mass fraction of saturated fatty acids, %			
	Lauric C12:0	Myristic C14:0	Palmitic C16:0	Stearin C18:0
Palm [5]	0.1	1.2–4.5	39.0–46.6	1.3–6.5
Palm oil	0.3	1.0	40.5	4.2
Palm stearin	0.3	1.5	61.1	4.8
Palm kernel	47.5	16.0	8.3	2.0
Cocoa butter	–	0.08	26.5	34.7
Coconut	47.0	18.5	8.8	3.0

However, saturated fatty acids must be in the human diet in the amount of 10 % of the daily caloric value to provide the body tissues with energy (β-oxidation). It is during the oxidation of saturated fatty acids that the body receives more than half of the energy it needs. This role, without harm to the body, can (only) stearic acid, according to WHO, does not affect the increase in low density lipoproteins in human blood plasma [6].

Secondly, the presence of esters of 3-monochloropropane-1,2-diol (E3-MCPD) and esters of glycidol (EG) in refined oils and their products. Their high content was found in refined palm oil [7, 8]. EGs are potential carcinogens due to the fact that they are readily hydrolyzed in the gastrointestinal tract, and have been found to induce tumors in various tissues of rats. In addition, glycidol is recognized by the International Committee as a «possible human carcinogen» (group 2A) [7]. According to the EU Commission Regulation 2020/1322, the EG content for edible fats placed on the market for the final consumer or for use as an ingredient in food products should not exceed the maximum allowable level of 1,000 μg/kg, and for E3-MCPD – 1250 μg/kg [9]. In Ukraine, the level of 3-MCPD in food is regulated by the regulations in accordance with [10] and is set at no more than 20 μg/kg. It has been proved that the mechanism of the formation of 3-MCPD esters is associated with the effect on triacylglycerols of hydrochloric acid, which was formed as a result of thermal decomposition of organochlorine compounds, and mono- and diacylglycerols are the precursors of the formation of esters of glycidol in fats when heated above 180 °C. Therefore, with the establishment of standards

ISSN 2664-9969

for the content of glycidol and 3-MCPD in food and the mechanisms of their formation, ways are formed to prevent their appearance during various technological processes, in particular refining, and during the cultivation of oilseeds [11].

Given this information, it can be assumed that fatty acids in their native form, triacylglycerols, are inconvenient both from the physiological and from the technological point of view. The growth of requirements for the quality of food products and fat and oil raw materials leads to the complication of technologies for their production and processing, and then the price of the final product grows. Let's propose an unconventional approach to solving the problems of the content of TFAL, EG and 3-MCPD esters, in which the appearance of these substances in modified fats disappears, and the modification technology is simple. This approach consists in converting triacylglycerols into ethyl esters of fatty acids [1].

Therefore, the esterification of stearic acid with ethyl alcohol is the only way to convert it into a form that is convenient for human consumption, that is, it allows to selectively introduce into the human diet those fatty acids that are very useful, as well as to exclude the appearance of FA trans isomers, esters of glycidol and 3-MCPD in food. In addition, ethylstearate is a unique product for the confectionery industry, which is confirmed by the qualitative assessment of chocolate products made on its basis.

It has been shown that in the manufacture of chocolate mass, replacement of cocoa butter with ethyl stearate in an amount of 33 % (in total in relation to the total amount of cocoa butter contained in cocoa products and added according to the recipe) does not affect the quality of confectionery products with standard and deviated from the standard storage conditions, namely the appearance of fatty «graying» on the surface of the product [12].

On the basis of the Kharkiv National Medical University, biomedical studies were carried out, confirming the possibility of using ethyl stearate in food.

For research, let's use ethyl stearate obtained by esterification of stearic acid (Germany) with ethyl alcohol (96 %) according to the method described in patent No. 143173 [13] and a commercial sample of cocoa butter.

The study of the melting and crystallization processes of ethyl esters of stearic acid at different heating and cooling rates (2 and 10 deg/min) was carried out using a DSC Q-20 TA Instruments differential scanning calorimeter (USA) according to [14].

The melting point and hardness of ethyl stearate were determined according to DSTU 4463.

The content of solid esters at 20 °C and 35 °C was determined by the method of pulsed nuclear magnetic resonance according to DSTU ISO 8292.

3. Research results and discussion

The results of thermal analysis (differential scanning calorimetry) for ethyl stearate at different heating and cooling rates are shown in Fig. 1, 2 and in Tables 2, 3. The analysis of the calorimetric curves showed that ethyl stearate crystallizes in a stable modification regardless of the crystallization conditions.

It is characteristic of glycerol esters that the melting point rises from an unstable modification to a stable one.

For example, in the case of tristearate, the melting temperature difference between alpha unstable and beta stable modifications is 7 °C [15]. The melting temperature of ethyl esters of stearic acid during rapid heating (10 deg/min) is higher than at slow heating (2 deg/min) and the difference is 1.8 °C, so it can be assumed that this is not due to the formation of stable and unstable modifications, but with the process of hypothermia.

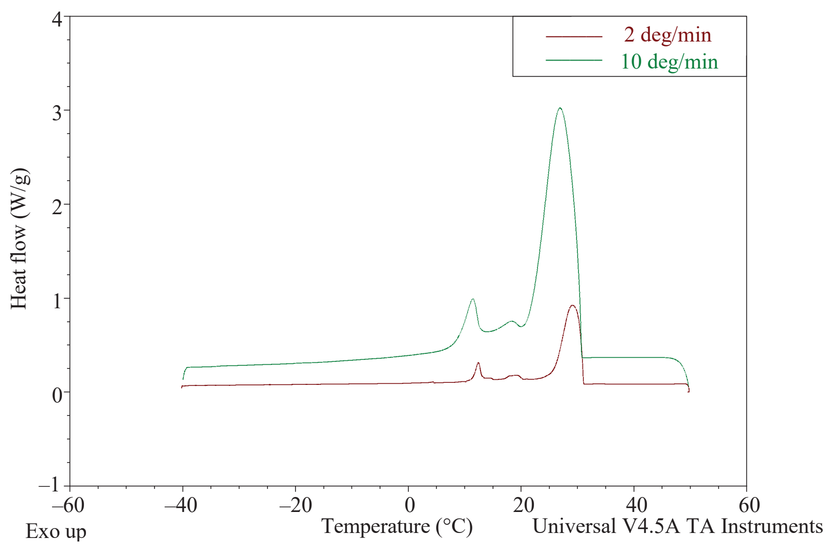

Fig. 1. Calorimetric crystallization curve for ethyl stearate

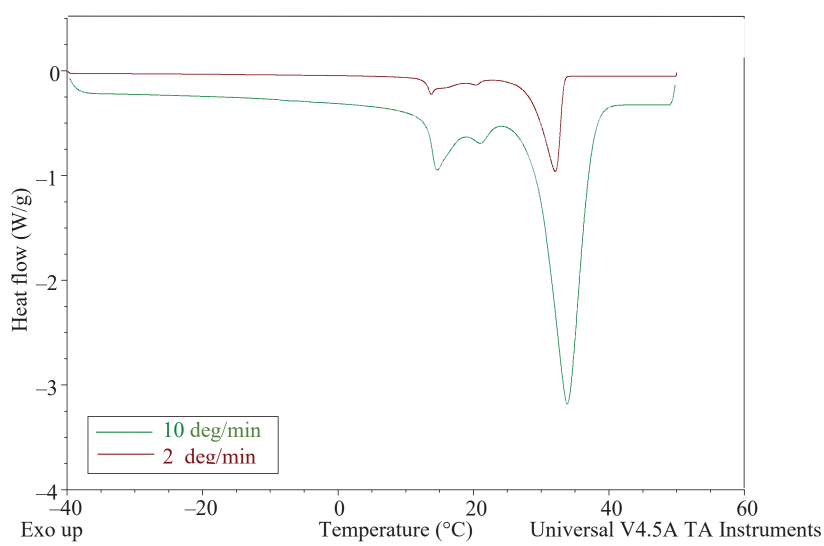

Fig. 2. Calorimetric melting curve of ethyl ether

Table 2

Indicators of the process of melting and crystallization of ethyl ether at a speed of 2 deg/min

Process	Start	Begin	Maximum	End	Area
	°C	°C	°C	°C	J/g
Melting	22.56	28.28	32.09	34.88	89.55
Crystallization	31.9	31.06	29.1	21.72	89.55

Table 3

Indicators of the process of melting and crystallization of ethyl ether at a speed of 10 deg/min

Process	Start	Begin	Maximum	End	Area
	°C	°C	°C	°C	J/g
Melting	23.89	29.01	33.84	42.08	86.31
Crystallization	31.09	30.71	26.98	20.1	86.74

To analyze the compatibility of ethyl stearate with cocoa butter, the melting point of the content of solid esters in ethyl stearate is 20 °C and 35 °C. The research results are shown in Table 4 and Fig. 3.

The values of the melting points (Table 4, Fig. 3) for ethyl stearate and its mixtures with cocoa butter indicate that they are mixed in any ratio.

Table 5 shows the content of solid esters in ethyl stearate in comparison with the content of solid fat in the equivalent of EFKO cocoa butter and cocoa butter at 20 °C and 35 °C.

Table 4

Melting points of mixtures of cocoa butter – ethyl stearate

Content of ethyl stearate in cocoa butter, %	Melting point, °C
100	33.4
90	31.6
50	29.5
10	27.6
0	27.0

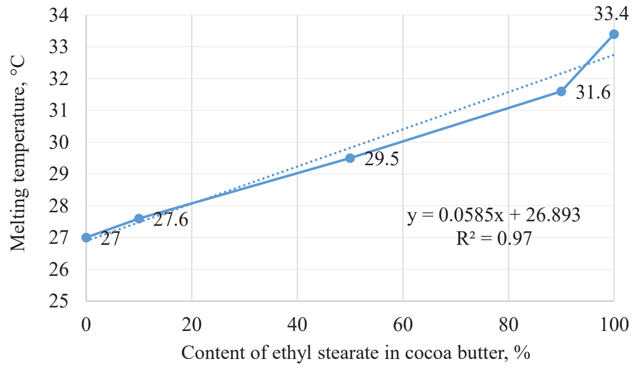

Fig. 3. Graph of the dependence of the melting point on the content of ethyl esters in cocoa butter

Table 5

Solid fat content in the test product

Name	Solid fat content at 20 °C, %	Solid fat content at 35 °C, %
Ethyl stearate	94.35	0.26
EFKO equivalent of cocoa butter	79.4	1.53
Cocoa butter	61.68	0

Ethyl stearate has a melting point not in the range, but at the point of 33.4 °C (with an experimental error), therefore, at a temperature from 20 °C to 33.4 °C, the content of solid esters in it is more than 90 %. Depends on the purity of the stearic acid and the degree of its conversion to ethyl esters.

The brittleness and hardness of ethyl stearate is similar to cocoa butter. Ethyl stearate hardness according to Kaminsky is more than 800 g/cm.

For comparison, the main physical and chemical indicators of natural cocoa butter, its alternatives and ethyl stearate are given in Tables 6, 7.

Based on the research results, it can be argued that ethyl stearate has physicochemical properties similar to cocoa butter and has a number of advantages over it and with the already existing alternatives to cocoa butter. Despite this, let's propose to amend the state standard (DSTU 5005), namely the addition of a new category of fats alternative to cocoa butter called «analog».

Table 6

Physical and chemical indicators of alternatives to cocoa butter according to DSTU 5005:2014 and ethyl stearate

Indicator	Cocoa butter alternatives				Ethyl stearate
	Equivalents	Improvers	Substitute	Surrogates	
Melting temperature, °C	No more than 33–36	No more than 36–45	No more than 32–40.5	No more than 32–44 (20–44)*	33.4
Solid triglyceride content, %, at temperature					
20 °C	No less than 65	–	72–96	60–98 (18–98)*	94.35
25 °C	No less than 50	–	55–85	40–95 (2–95)*	–
30 °C	No less than 32	–	29–60	18–60 (0–60)*	–
35 °C	No more than 9	No more than 6	0–30	No more than 18	0.26
Cocoa butter compatibility, %	0–100	0–100	0–20	0–5	0–100

Note: * – for ice cream frosting

Table 7

Physical and chemical indicators of cocoa butter according to DSTU 5004:2008 (2017)

Indicator	Norm
Melting point, °C	32–35
Solid fat content, %	No less than 65
Pour point, °C	No less than 25

The production and use of ethyl stearate as a new alternative to cocoa butter will allow the resumption of the export of those food products that did not meet European and world standards in terms of safety indicators and the TFAI content. Ethyl stearate-based food ingredients help improve human health, since ethyl esters are the most convenient form for consumption of stearic acid, which is better absorbed and unlike other saturated acids and does not affect the CVD development. Hydrolytic degradation of ethyl stearate in the body probably does not lead to the resynthesis of fat that occurs during hydrolysis of triacylglycerols. The technologies for the ethanolysis of fats and the esterification of fatty acids are easier to implement in comparison with the technologies of modified fats like cocoa butter. In addition, special-purpose fats can be obtained by partially or completely converting triacylglycerols into ethyl esters of fatty acids. For this category of lipid products, the technical conditions TU U 20.5-1225000194-001:2019 «Modified vegetable confectionery, culinary, bakery and dairy fats» have been developed and approved in accordance with the established procedure.

4. Conclusions

The physicochemical properties of ethyl stearate as a new alternative to cocoa butter have been determined, namely:

– melting point at the point (33.4 °C);
– content of solid esters 20 °C 94.35 %;
– mixes up with cocoa butter in any ratio;
– high hardness (more than 800 g/cm);
– absence of trans fatty acid isomers.

Considering these properties, as well as the facts that trans fatty acid isomers are not formed during the production and use of ethyl stearate, it is recommended to add ethyl stearate to DSTU 5005 esters of glycidol and 3-MCPD as a new alternative to cocoa butter.

It has been proven that stearic acid, the only saturated fatty acid, does not affect the increase in LDL, it is suitable for human consumption only in the form of ethyl ester. Thus, ethyl stearate can meet the human need for healthy and safe saturated fatty acids, which must be present in the human diet.

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