

“LIPIDS MIMETICS” WITH MONITORISED HLB VALUES AND HOMOGENOUS β -LAURYL/MYRISTYL (7/3) POLYETHYLENEOXY ($\bar{n} = 0-20$) PROPIONIC ACIDS IN TOMATOES AND PLUMS

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ABSTRACT – *The aim of the paper was to analyse the possibility of developing the range of fat substitutes (FS) as potential ingredients, or products of foodstuff additives with controlled functioning. The paper focused on the study of the impact of process parameters on esterification and/or transesterification process structure, yields and selectivity. The controlled modification of the polyoxyethylene chain ($\bar{n} = 0-20$) (PEO) allowed us getting polyunsaturated fatty acids from plums (*Prunus domestica* Damascena) and tomatoes (*Solanum lycopersicum*) with favourable impacts on their major colloidal characteristics (dispersants, antifoaming agents, emulsifiers, solubility agents, humectants, etc.). The materials and reactives used in this work were β - lauryl/ miristyl (7/3) polyethylenoxi ($\bar{n} = 0-20$) propionic acids, different vegetal oils (tomatoes and plum); anhydrous glycerin p.a., strong mineral acid (H_2SO_4). The lipid fractions obtained and suggested as FS were purified, chemically and physically/chemically characterized, in order to establish the potential use in foodstuff processing. The results were presented in three tables: dependence of the acid value (mg KOH/g product) in the process of esterification of the β -lauryl/miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids and of their esters, in relation to temperature, in acid catalysis; dependence of the acid value (mg KOH/g product) in the process of esterification of the β -lauryl/miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids and of their esters in relation to the molar ratio glycerin/ acid; dependence of the acid value (mg KOH /g product) in the process of esterification of the β -lauryl/ miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids and of their esters, related to time processing.*

Key Words: glycerides of the β -lauryl/miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids, fat substitutes, foodstuff additives

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REZUMAT - Înlocuitori lipidici cu valori HLB monitorizate și caracterizarea unor structuri lipidice cu acizi β -lauril/miristol (7/3) polietilenoxi ($\bar{n} = 0-20$) propionici omogeni și acizi superiori din semințe de tomate și prune. Lucrarea și-a propus să analizeze posibilitățile de diversificare a gamei de lipide structurate (LS) ca potențiale ingrediente sau produse de aditivare alimentară cu funcții de control. Studiile s-au focalizat asupra dependenței parametrilor de procesare, funcție de procesele de esterificare și/sau transesterificare, structură, randament și selectivitate. Modificarea controlată a catenelor polioxieterilenice ($\bar{n} = 0-20$) (PEO) a permis obținerea de acizi superiori polinesaturați hidrofilii din sămburi de prune (*Prunus domestica* Damascena) și semințe de tomate (*Solanum lycopersicum*), cu impact favorabil asupra majorității caracteristicilor coloidale (dispersanți, agenți antispumare, emulgatori, agenți de solubilizare, umectanți etc.). Materialele și reactivii utilizați în această lucrare au fost: acizi β -lauril/miristol (7/3) polietilenoxi ($\bar{n} = 0-20$) propionici, diferite uleiuri vegetale (semințe de tomate, sămburi de prune); glicerină anhidră p.a., acid mineral puternic (H_2SO_4). Frațiunile lipidice obținute și recunoscute ca LS au fost purificate, caracterizate chimic și fizico-chimic, pentru a stabili potențialele utilizări în procesarea agro-alimentară. Rezultatele au fost prezentate în trei tabele: dependența indicelui de aciditate (mg KOH/g produs) în procesul de esterificare a acizilor β -lauril/miristol (7/3) polietilenoxi ($\bar{n} = 0-20$) propionici și a esterilor lor de temperatură, în cataliză acidă; dependența indicelui de aciditate (mg KOH/g produs) în procesul de esterificare a acizilor β -lauril/miristol (7/3) polietilenoxi ($\bar{n} = 0-20$) propionici și a esterilor lor de raportul molar glicerină/acid; dependența indicelui de aciditate (mg KOH/g produs) în procesul de esterificare a acizilor β -lauril/miristol (7/3) polietilenoxi ($\bar{n} = 0-20$) propionici și a esterilor lor de durata de procesare.

Cuvinte cheie: gliceride ale acizilor β -lauril/miristol (7/3) polietilenoxi ($\bar{n} = 0-20$) propionici, înlocuitori lipidici, aditivi alimentari

INTRODUCTION

Foodstuff fat substitutes (FS) represent an ancient concern, signaled in literature. Their protein, lipid or glucide nature was determined by foodstuff processing. Esters, generally, and glycerides, particularly, in simple and complex mixtures (E-430→E-436; E-471→E-482) have confirmed, since the beginning of food processing, their role as basic nutritive principles, and recently they have also confirmed their beneficial effects as foodstuff additives (emulsifiers, stabilizers, moisturizing agents, sequestrants, etc.). Recently, in the dispute pro and against their role in controlling the functional nutrition, they have also gained new functional abilities as **fat substitutes (FS) of lipid nature**. The diversifying idea was suggested by the encouraging results obtained by the synthesis of the **β -alkyl (C_{12} - C_{18}) polyethylenoxy ($n=0-20$) acetic and propionic acids**, or by condensing industrially **polyethoxylate ($n=0-20$) high alcohols (C_{12} - C_{18}) with monochlor acetic acid** i.e., by nucleophilous addition in the basic catalysis of the same structures to acrylnitrile, followed by partial and total acid hydrolysis. Not only the toxicity tests in literature and advanced purity of synthesis products, but also the capacity of adapting the HLB balance by controlled modification of

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polyoxyethylene chain (PEO) suggested the idea of getting new glycerides (mono-, di-, and tri-) by direct esterification or by transesterification (*Figure 1*). Inevitably, the final product will have the qualities of a complex structure mixture. Chemical and physical-chemical characterization represented an important step in the effort of further defining its used values (Yamagida et al, 1978).

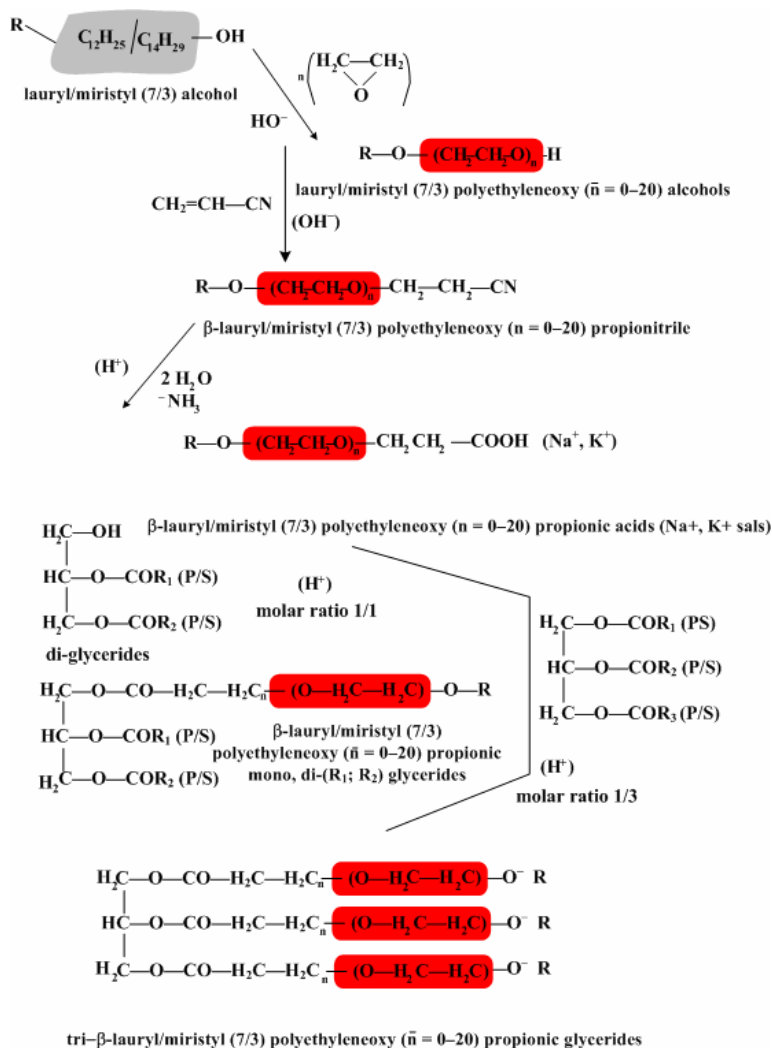


Fig. 1 - Processing methods by esterification and transesterification of glycerides with β-lauryl/miristil (7/3) polyethyleneoxy ($\bar{n} = 0-20$) propionic acids

The balance deviation to the advantage of esters and glyceride formation depends on lowering water concentration or even on its removal from the system. If water removal is not possible (alcohol miscible with water), the deviation of the balance can be achieved by adding in excess one of the processing components — glycerin.

Removing water from the system can be practically done in case of immiscible alcohols and by distillation with an immiscible solvent with or without alcohol and/or acid recirculation, if its volatility allows the protection, under working conditions that do not affect the quality of the final product. In this study, we have used glycerin (as alcohol miscible with water).

In the indirect esterification variant, the process mixture also includes the fatty acid fraction, present in the structure of the glyceride, using as raw material tomatoes and plum-oil, etc. We have processed their transesterification in accordance with the adapted classical process scheme (*Figure 1*) (Vögtle et al., 1977).

This paper studied the influence of process parameters on structure, yields and selectivity of the esterification and/or transesterification process. Lipid fractions proposed as potential FS were afterwards purified, chemically and physically-chemically characterized, in order to establish the potential use in foodstuff processing.

The controlled modification of the homogenous polyoxyethylene chain ($n = 0-20$) PEO allowed the proper regulation of hydrophilic characteristics, of the final HLB value of SF with favourable consequences on their major colloidal characteristics (dispersants, anti-foaming agents, emulsifiers, mycelial solubility agents, moisturizers, etc.). Foodstuff processing is interested in the large offer of foodstuff additives with controlled HLB balances, similar to other classical foodstuff additive structures ($E - 431 \rightarrow E - 436$; $E - 430 \rightarrow E - 431$) (Shinoda, 1976; Longmann, 1975).

MATERIALS AND METHODS

Materials and reactives: β -lauryl/miristyl (7/3) polyethylenoxi ($\bar{n} = 0-20$) propionic acids; different vegetal oils (tomato and plum); anhydrous glycerin p.a. (Merck); strong mineral acid (H_2SO_4).

Method of work: We introduced in a three-neck reaction vessel endowed with efficient stirring, thermometer and cooler 0.1 mols of lipid fraction recuperated from vegetal by-products (the equivalent molecular weight was determined by chromatography in the gas phase of the vegetal lipid fractions).

We have added, under continuous stirring, the acid catalyst (H_2SO_4) of 3–5 %, as compared to the oil under work, and afterwards the β -lauryl/miristyl (7/3) polyethylenoxi ($\bar{n} = 0-20$) propionic acids (molar ratio 1/1; 1/3) (*Table 1*).

We heated the processing mixture up to 80–160°C and kept stirring for a few hours. The fluid product got darker more or less according to the working temperature. In this case, there is a stronger change in colour, with formation of light brown solid

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suspensions. We wash twice the product obtained (fluid, paste and wax) with 100 mL of 60–70°C water, by mechanical stirring (in order to avoid emulsification), afterwards, we collect water residues. The final ester (after purification) was evaluated by current chemical analyses (acid value, saponification, ester and iodine value, IR spectra, etc.). Yields reported in the glyceride found in the process, between 85 and 95 %, were calculated by determining saturated and unsaturated acids from washing waters (chromatograms in the gas phase of methyl esters) that were compared with their distribution in the initial raw material in the process of transesterification. In order to evaluate quantitatively, the raw product was washed and then purified by repeated liquid-liquid extractions (**, 1976; ** 1964).

Table 1

Acid value (calculated and determined) of the β -lauryl/miristyl (7/3) polyethylenoxi (\bar{n} = 0–20) propionic acids

Oligomer degree (\bar{n})	Molecular weight (\bar{M})	I_A [mg NaOH (KOH)/g acid]	
		as NaOH	as KOH
\bar{n} =0	174	228.09/229.88	321.90/321.84
\bar{n} =3	306	131.38/130.72	182.49/183.00
\bar{n} =6	438	92.49/91.32	126.02/127.85
\bar{n} =9	570	71.58/70.17	97.03/98.25
\bar{n} =12	702	57.82/56.98	78.58/79.77
\bar{n} =16	874	46.87/45.77	65.84/64.08
\bar{n} =20	1054	38.49/37.95	52.44/53.13

¹ free of high alcohol and PEG

RESULTS AND DISCUSSION

In all cases, at a temperature over 80°C, the content in β -lauryl/miristyl (7/3) polyethylenoxi (\bar{n} = 0–20) propionitrile decreased steadily, no matter the acid catalyser used. We might also notice the presence of propionic esters. Meanwhile, the content in propionic ester has increased once with the decrease of polyoxyethylene chain length in the polyethoxylate high alcohol that had to be introduced (\bar{n} = 3–9).

The results obtained allowed the assessment of the individual content in mono-, di-, and tri-glycerides in the processing mixture, and of the distribution of β -lauryl/miristyl (7/3) polyethylenoxi (\bar{n} = 0–20) acids, in relation with hydrophilous chain size in transesterification and esterification of various glycerine hydroxyl groups (Tables 2, 3, 4).

Table 2

The dependence of the acid value on temperature (mg KOH/g product) in the process of esterification of the β -lauryl/miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids and of their esters in acid catalysis

No.	\bar{n}	Temperature (°C)	Conversion (%)
1	0	110	48.18
2	↑ 3	110	↑ 54.32
3	↑ 6	110	↑ 59.05
4	↑ 9	110	↑ 61.09
5	↑↑ 20	110	↑ 71.47
6	9	↑ 130	↑ 64.55
7	9	↑ 150	↑ 69.88
8	9	↑ 160	↑ 72.71

Table 3

The dependence of the ratio molar glycerin/acid of the acidity value (mg KOH/g product) in the process of esterification of the β -lauryl/miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids and of their esters

No.	\bar{n}	Ratio glic./LM(PEO) _n PC	Conversion (%)
1	9	↑ 1/1	↑ 69.04
2	9	↑ 1/1.1	↑ 71.11
3	9	↑ 1/1.3	↑ 75.52
4	9	↑ 1/1.5	↑ 79.67
5	9	↑ 1/2	↑ 81.81
6	↑ 20	↑ 1/1.3	↑ 79.04
7	20	↑ 1/1.5	↑ 82.52
8	20	↑ 1/2	↑ 89.67

Table 4

Dependence on the acid value processing duration (mg KOH/g product) in the process of esterification of the β -lauryl/miristyl (7/3) polyethylenoxy ($\bar{n} = 0-20$) propionic acids and of their esters

No.	\bar{n}	Temperature (°C)	Conversion (%)
1	9	1	71.18
2	9	↑ 1.5	↑ 74.32
3	9	↑ 2	↑ 77.08
4	9	↑ 2.5	↑ 79.05
5	9	↑ 3	↑ 82.49
6	↑ 20	↑ 2	↑ 79.61
7	20	↑ 2.5	↑ 81.82
8	20	↑ 3	↑ 89.93

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CONCLUSIONS

These results allowed us to continue the investigations in strict relation with the interest for the practical utility in foodstuff processing, together with the study of basic colloidal properties.

Over 80°C, the content in β -lauryl/miristyl (7/3) polyethylenoxi ($\bar{n} = 0-20$) propionitrile decreases steadily, no matter the acid catalyser used, being noticed the presence of propionic esters and supporting the validity of proceedings applied in the experiment.

The analysis of experimental data resulted from the total acid hydrolysis of β -lauryl/miristyl (7/3) polyethylenoxi ($\bar{n} = 0-20$) propionitriles synthesized has shown the incipient presence of the esters, in limited amounts, ever since this phase.

REFERENCES

- ***, 1976 - *American Society Testing Materials. Standards on Soap and other Materials*, American Chemical Society, Philadelphia
- ***, 1964 - *Methods of sampling and testing detergents (British Standards) B.S. 3762*, British Standards institutions, London
- Longmann G., 1975 - *The Analysis of Detergents and Detergents Products*, John Wiley & Sons, New York, Chichester
- Shinoda R., 1976 - *Solvent Properties of Surfactants Solution*, Marcel Dekker Press, New York
- Vögtle F., Sieger I.H., 1977 - *Angew. Chem. (Internal Ed.)*, 16, 396
- Yamagida S., Takahashi K., Okahara I.M., 1978 - *Bull. Chem. Soc., Japan*, 51(5), 1294