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(72) **Inventeurs/Inventors:**
ZAJAC, TADEUSZ STANISLAW, PL;
ZAJAC, PIOTR, PL;
ZANDER, ZYGMUNT, PL;
ZANDER, LIDIA BOZENA, PL;
DAJNOWIEC, FABIAN JULIAN, PL;
BANASZCZYK, PAWEL, PL

(73) **Propriétaire/Owner:**
3L INVENT SP. Z O. O., PL

(74) **Agent:** AVENTUM IP LAW LLP

(54) **Titre : DENREE ALIMENTAIRE BENEFIQUE POUR LA SANTE CONTENANT DES ESTERS D'HUILE DE LIN ET PROCEDE POUR L'OBTENIR**

(54) **Title: HEALTH-GIVING FOODSTUFF CONTAINING ETHYL ESTERS OF LINSEED OIL AND METHOD FOR OBTAINING THE SAME**

(57) **Abrégé/Abstract:**
A health-giving foodstuff containing ethyl esters of fatty acids of linseed oil is provided. The foodstuff is constituted of microcapsules in a form of powder, which contains, in a protein-carbohydrate matrix, a nutraceutical with bioactive ethyl esters of acids ALA (α-Linolenic acid) and LA (Linoleic acid) in a form of drops of diameter less than 2 µm. Not more than 4 percent by weight addition of ethanol, based on at least 99,8% anhydrous pharmaceutical ethanol, is present. In the protein-carbohydrate matrix the proteins are derived from milk proteins concentrates with decreased lactose concentration, containing a minimum 30 percent by weight of proteins and/or plant proteins concentrates, and the carbohydrates are derived from low saccharification maltodextrin with DE index not higher than 13.

ABSTRACT

A health-giving foodstuff containing ethyl esters of fatty acids of linseed oil is provided. The foodstuff is constituted of microcapsules in a form of powder, which contains, in a protein-carbohydrate matrix, a nutraceutical with bioactive ethyl esters of acids ALA (α-Linolenic acid) and LA (Linoleic acid) in a form of drops of diameter less than 2 μm. Not more than 4 percent by weight addition of ethanol, based on at least 99,8% anhydrous pharmaceutical ethanol, is present. In the protein-carbohydrate matrix the proteins are derived from milk proteins concentrates with decreased lactose concentration, containing a minimum 30 percent by weight of proteins and/or plant proteins concentrates, and the carbohydrates are derived from low saccharification maltodextrin with DE index not higher than 13.

Health-giving foodstuff containing ethyl esters of linseed oil and method for obtaining the same

FIELD OF THE INVENTION

The subject of the invention is a health-giving foodstuff containing ethyl esters, of linseed oil and method for obtaining the same.

BACKGROUND

PL 201 959 presents a method for obtaining of health-giving dairy products and health-giving food dairy product.

The method consists in that after initial milk processing, specific for a defined product, there is added 3 to 10% of a milk-oil emulsion made of milk and oil composition containing polyunsaturated fatty acids, namely omega-3, preferably docosahexaenoic acid - DHA and/or eicosapentaenoic acid - EPA, to a prepared in known way raw material and/or a semi-finished dairy product suitable for an obtained product. The emulsion is homogenised at temperature 60-70°C and pressure of at least 15 MPa. Polyunsaturated fatty acids are usually of natural origin. Then, there is added an anti-oxidative vitamins A, C, E composition in form of a solution and at amount justified by nutrition and physiology, followed by technological processing of the emulsion and the combination which is necessary for obtaining a defined product, and, depending on needs, there are added known additives, namely stabilizing salts and thickeners, powdered milk and flavours at adequate stage of the product manufacturing.

The health-giving dairy product is characterised by that it contains the milk-oil emulsion prepared with oils containing polyunsaturated fatty acids, namely of omega-3 group, preferably of natural origin and it contains the composition of anti-oxidative vitamins, particularly A, C, E vitamins and known additives, particularly stabilizing salts, thickeners, powdered milk and flavours at amounts justified by technology.

PL 203 686 disclosures a feed additive, method for manufacturing of the feed additive, feed composition containing the feed additive and usage of the feed

additive in feeds.

The feed additive containing chemical compounds with unsaturated acid radicals is characterised by that it contains fatty acids salts, at least of linseed oil, with metals of 1 and/or 2 group of the periodical table or preferably $NH4^+$, in which ratio of salts of polyunsaturated fatty n-6 acids to n-3 ones is 0,1 -1,0 : 1.

The method for obtaining of the feed additive consist in that a fat emulsion, preferably of linseed oil in water, is treated with oxides or hydroxides of metals of 1 and/or 2 group of the periodic table or preferably with $NH4^+$ at room temperature, or preferably with $NH4^+$ at temperature elevated up to boiling point and at stoichiometric or larger amount of a metal oxide or hydroxide or ammonium hydroxide. Obtained precipitate is filtrated, washed out with water and dried, and the obtained fatty acids salts are incorporated into a final product, preferably together with anti-oxidants.

Feed composition with the feed additive, comprising of a feed and other nutritious products and/or other materials used in nutrition of commercial animal herds is characterised by that it contains from 4-12 percent by weight of the feed additive in a powdery form and which consist of fatty acids salts, at least of linseed oil with metals of 1 and/or 2 group of the periodic table or preferably $NH4^+$, in which ratio of salts of n-6 polyunsaturated acids to n-3 ones is 0,1-1,0 : 1. The prepared composition for animals feeding with the feed additive contains polyunsaturated fatty acids and metal and/or ammonium salts of these fatty acids of n-6 to n-3 at ratio 2-6:1. The feed additive contains salts of conjugated linoleic acids with metals of 1 and/or 2 group of the periodic table or preferably $NH4^+$ at amount of 40 percent by weight of a dry mass of the feed additive.

Use of the feed additive is foreseen in rearing animals at the end of fattening period with addition of the additive at amount of 4-12 percent by weight of a dry mass of the feed additive.

PL P386607 describes a nutritional additive, method for its manufacturing and the installation for implementation of this method, and the use of the nutritional additive manufactured by this method. The nutritional additive consists of active

substances, particularly of polyunsaturated fatty acids in form of a concentrate of saturated and unsaturated ethyl esters of long-chain fatty acids, namely of linseed oil. Furthermore, the nutritional additive consists of active substances, namely polyunsaturated essential fatty acids in form of ethylamids of long-chain fatty acids, namely of linseed oil. Also, the nutritional additive consists of active substances, namely of polyunsaturated fatty acids in form of a mixture of concentrate of ethyl esters of long-chain fatty acids, namely linseed oil, and of ethylamids of long-chain fatty acids, namely of linseed oil constitute the nutritional additive.

The method for obtaining of the nutritional additive consists in a process of transesterification of esters with glycerides of raw oil, namely linen oil with 16- to 18- fold excess of directly dehydrated, pharmaceutical ethanol (anhydrous) of concentration at least 99,8% and with a catalyser - ethanol solution of alkali metal hydroxide, for example of potassium hydroxide, conducted in oxygen-free atmosphere saturated with gaseous nitrogen up to balance state with protected clean in order to protect from humidity, carbon dioxide and atmosphere oxygen, at preferably room temperature by effective homogenisation of the reaction mixture resulting from mixing with ejectors supported by circulation pumps with protection of spherical conformation c/s of fatty acids. Then, at least one-step distillation of unreacted ethanol is carried out under underpressure of at least 95 kPa and at maximal temperature of 80°C vapour condensation by a coat-like condenser and separation of the remaining mixture to ester and glycerol phases followed by purification of the ester phase undergoes further processing. The final product is dispensed and transferred to a warehouse.

CN 101 940 240 A (DATABASE WPI Week 201128, Derwent Publications Ltd., London, GB; AN 2011-C47647, XP002681997) describes a method for preparing a fish oil ethyl ester microcapsule from fish pomace, which mainly comprises the extraction of fish oil, the preparation of fish fatty acid ethyl ester, the purification of fish oil ethyl ester and the preparation of a fish oil ethyl ester microcapsule, wherein the extraction of fish oil comprising the following steps: eliminating foreign matters from fish viscus, cleaning, mashing, adding pepsin and neutral protease for enzymolysis, then adding anhydrous alcohol, standing to stratify, and centrifuging to obtain the fish oil; the preparation of fish fatty acid ethyl ester

comprising the following steps: mixing the fish oil with ethanol, making the mixture to be subject to an esterification reaction under the catalysis of sodium ethylate, vaporizing the ethanol, washing with water and then centrifuging to obtain the fish oil ethyl ester; in the purification process, supercritical CO_2 extraction is adopted, the purified fish oil ethyl ester is a golden yellow transparent liquid, and EPA ethyl ester and DHA ethyl ester contents thereof are more than 50%; and the preparation of a fish oil ethyl ester microcapsule comprises the following steps: mixing sodium alginate, maltodextrin and sodium caseinate, dissolving in water, adding the purified fish oil ethyl ester, and adopting a spray drying method to obtain the powdered fish oil ethyl ester microcapsule which can hide the fishy smell of the fish oil ethyl ester, improve the mouth feel and be beneficial to packaging and storage.

CN 101 669 920 A (DATABASE WPI Week 201031, Derwent Publications Ltd., London, GB; AN 2010-D58326, XP002681998) relates to a strong anti-oxidation DHA microcapsule. The microcapsule comprises the following components in percentage by weight: 10 to 30 percent of DHA fish oil, 0,02 to 0,2 percent of antioxidant, 10 to 60 percent of wall material, and 5 to 30 percent of auxiliary wall material. The invention also relates to a method for preparing the strong anti-oxidation DHA microcapsule. On the basis of the prior process, the microcapsule is prepared by adding the antioxidant to oil phase and water phase respectively and performing emulsification, high-pressure homogenisation, improved spray granulation and cold-air boiling-drying. The newly added antioxidant can produce better anti-oxidation effects and greatly improve the oxidation stability of the DHA microcapsule so as to prolong the shelf life of products, and the improved spray granulation and the cold-air boiling-drying process can increase the yield of the DHA microcapsule. The DHA microcapsule can be used in the fields of medicines, foods, beverages and the like.

US 2004 017017 A1 (Van Lengerich Bernhard H. et al.) describes a stabilized emulsion is employed to produce shelf stable, controlled release, discrete, solid particles or pellets which contain an encapsulated and/or embedded component such as a readily oxidisable component, such as omega-3 fatty acids. An oil encapsulant component which contains an active, sensitive encapsulant dissolved

and/or dispersed in an oil is admixed with an aqueous component and a film-forming component to form an emulsion. An antioxidant for prevention of oxidation of the active, sensitive encapsulant and a film-softening component or plasticizer for the film-forming component may be included in the emulsion. The emulsion is stabilized by subjecting it to homogenisation. The pellets are produced by first reducing the water content of the stabilized emulsion so that the film-forming component forms a film around the oil droplets and encapsulates the encapsulant. In embodiments of the invention, the water content of the homogenised emulsion may be reduced by spray-drying to produce a powder. In other embodiments of the invention, after homogenisation the water content of the emulsion may be reduced by admixing the emulsion with at least one matrix material to thereby encapsulate the film-coated oil droplets within the matrix material. After the water content of the emulsion is reduced, a protective coating is applied on the film-coated oil droplets to obtain pellets.

SUMMARY

The problem to be solved and the aim of the invention is to obtain of a health-giving foodstuff containing a concentrate of ethyl esters of fatty acids, namely of linseed oil, as a nutraceutical, as well as development of its obtaining method.

Due to the fact that the ethyl esters are in form of oily, strongly hydrophobic liquid with specific taste and smell, which makes their use inconvenient, there has been considered a change of the ester form to a solid form powder. It has been also considered an increase of nutritional value of a product and maintenance its health-giving properties.

It became necessary to ensure microbiological purity of the powder composed only of edible components and totally free of toxic substances.

It was found that the bioactivity and microbiological purity of ethyl esters of acids ALA and LA can be used.

The aim and the problem of the invention is solved by the health-giving foodstuff containing ethyl esters of fatty acids of linseed oil characterised in that it is constituted of microcapsules in a form of powder, which contains, in a protein-

carbohydrate matrix, a nutraceutical with bioactive ethyl esters of acids ALA (α-Linolenic acid) and LA (Linoleic acid) in a form of drops of diameter less than 2 µm, with not more than 4 percent by weight addition of ethanol based on at least 99,8% anhydrous pharmaceutical ethanol, wherein in the protein-carbohydrate matrix as proteins there are used milk proteins concentrates with decreased lactose concentration, containing minimum 30 percent by weight of proteins and/or plant proteins concentrates, wherein in the protein-carbohydrate matrix as carbohydrate there is used low saccharification maltodextrin with DE index not higher than 13.

Microcapsules diameter is 20 - 270 µm. The protein-carbohydrate matrix contains minimal amount up to 5 percent by weight flavouring-colouring additives such as β-carotene, lemon juice, orange juice, aromas and colourings, vitamins, bio-elements and optionally, addition of soya lecithin up to 2 percent by weight.

A method for obtaining a health-giving foodstuff containing ethyl esters of fatty acids of linseed oil, by mixing of ingredients, their homogenisation, drying, characterised in that after obtaining a liquid protein-carbohydrate matrix, a nutraceutical containing bioactive ethyl esters of acids ALA (α-Linolenic acid) and LA (Linoleic acid) is introduced into it, followed by carrying out a dispergation of the ester phase by mechanical agitation until a stable form of emulsion is obtained, which is then treated with two-steps and two-stages pressure homogenisation: at pressure of 20 MPa - 25MPa in a first step of a first stage and 4 MPa - 5MPa in a second step of the first stage at a temperature of 50-70°C, and at pressure of 30 MPa - 60MPa at a temperature of 40-70°C in a first step of a second stage and at pressure of 10 MPa -15 MPa at a temperature of 50-70°C in a second step of the second stage, whilst homogenisation during the first stage is carried out in a process coupled with thermal processing of the emulsion, which is then spray dried in atmosphere at a temperature 160-190°C in an inlet of a drying cabinet to produce a powder and the powder is dispensed in a neutral gas atmosphere.

After homogenisation of the 1st stage and before homogenisation of the 2nd stage, the emulsion may be put aside for 6 hours, and after that may be warmed up to 50 - 70°C.

A continuous phase of the emulsion is obtained, preferably, by dissolving in water of temperature about 30°C the matrix components, that is proteins and polysaccharides, followed by protein hydration and the nutraceutical is introduced after hydration of the components. The protein hydration is carried out at temperature 25-35°C for about 4 hours.

During thermal processing the stable emulsion is, preferably, warmed up to temperature about 50 - 65°C, pasteurised and cooled down to about 10°C.

During storage and dispensing of the health-giving foodstuff may be carried out in nitrogen as a neutral gas atmosphere.

The health-giving foodstuff in form of a powder is as well absorbed by living beings as nutraceutical as such, which can pelletized, encapsulated or use for production of butter, cheese, fermented dairy drinks, sausages, baker's goods, pastas, and in addition it has higher nutritive value as it is enriched by proteins and carbohydrates if microcapsules matrix. It creates more possibilities of its usage as a diet supplement / food supplement / enriched foodstuff as a component of substances both in liquid and solid form, because structure of inside allows its reproduction in form of emulsion, conveniently with concentration of the ingredients from 35 - 45%.

BRIEF DESCRIPTION OF THE DRAWINGS

The nutraceutical structure and the health-giving foodstuff in form of microcapsules are presented on microscope pictures enclosed to this description.

Fig. 1. It presents emulsion of ethyl esters of fatty acids of linseed oil after repeated two-step pressure homogenisation microcapsules after dissolving. Ester drops form a stable emulsion without tendency to coalescence, in spite of predisposition to flocculation. Diameter of the ester drops does not exceed 2 μm. The picture was taken from an optical microscope under magnification of 40x.

Fig. 2. It presents microcapsules in form of powder after spray drying of microcapsule dimensions 20 - 270 μm. The picture was taken with an electron microscope at magnification 1600x.

DETAILED DESCRIPTION

Microbiological quality of the health-giving foodstuff is comparable with powdered milk for babies. It has neutral taste and there is no smell specific for esters.

In the method according to this invention there are used only edible components of natural origin, and no emulsifiers obtained by chemical synthesis and in this way thermal and chemical disintegration of raw materials is avoided. As a consequence of two-stage and two-step pressure homogenisation there is achieved guaranty of closure of the bioactive substance - ethyl esters of acids ALA, LA inside structure of powder particles. Dehydration of microcapsules matrix by skillful spray drying makes impossible microorganisms growth inside the microcapsules as result of drastic decrease of water activity.

The inventions is closer explained in the examples showing composition of dry mass of the health-giving foodstuff expressed in percent by weight and method for obtaining the same.

Examples

The subject of the invention is shown closer in preferred examples of its realisation. The examples of realisation shall not be considered in any case as an exhaustive and limiting the presented inventions, and which nature has been characterised in patent claims.

Example 1

- low-saccharification maltodextrin DE 7-13: 50,0 percent by weight
- milk protein concentrate MPC 75: 16,7 percent by weight
- ethyl ester of acids ALA and LA: 33,3 percent by weight

Example 2

- low-saccharification maltodextrin: 50,0 percent by weight
- soya protein isolate: 20,0 percent by weight
- ethyl ester of acids ALA and LA: 30,0 percent by weight

Example 3

During mixing, to 40 dm^3 of water warmed up to about 30°C there are added 30,5 kg of low-saccharification maltodextrin DE 7-13, 10 kg of soya protein isolate and 25 dag of lecithin. After dispersing of the ingredients, the obtained emulsion is put aside for 5 hours at temperature of about 30°C in order to protein hydration. Then, during the continuous mixing, there is added 19,5 kg ethyl esters available under commercial name LeenLife E and all of them is still mixing until stable emulsion isobtained. The obtained stable emulsion is thermally treated, which includes: warming up to temperature of 40°C, pasteurisation at 70°C, and cooling down to 9°C in a cycle coupled with process of pressure homogenisation at temperature of about 50°C at pressure about 23 MPa at the first step and about 5 MPa on the second step.

After achieving drops of esters of diameter up to 6 μm, the emulsion is transferred to the second stage of the pressure homogenisation at pressure about 47 MPa at the first step and about 15 MPa at the second step. Then, after achieving drops of esters with a diameter up to 1 μm, the emulsion is directed to spray drying in a stream of hot air of temperature about 190°C at inlet and about 90°C at outlet of a dryer. There are obtained 58 kg of the health-giving foodstuff according to the invention.

Example 4

During mixing, to 66 dm^3 of water warmed up to temperature of about 35°C there is added 18 kg of low-saccharification maltodextrin DE 7-13, and 6,2 kg of milk protein concentrate MPC 75 and addition of 30 dag of lemon juice. After dissolution of the ingredients, the obtained emulsion is put aside for 3 hours at temperature of 30-20°C in order to hydrate proteins. Then, during mixing, there is added 12,1 kg of ethyl esters available under brand name LeenLife E and there is carried out dispersion of ester phase by mixing. The obtained stabile emulsion is treated thermally: warming up to 45°C, pasteurisation 70°C and cooling down to 10°C in cycle coupled with the first stage of pressure homogenisation at temperature about 55°C at pressure about 23 MPa at the first stage and about 4 MPa at the second stage.

After achieving drops of esters having a diameter less than 6 μm, the emulsion is left for 3 hours at temperature 10°C. After warming up to about 50°C, the emulsion is directed to pressure homogenisation at pressure 45 MPa at the first step and 14MPa at the second step. Then, after achieving some drops of esters with a diameter smaller than 2 μm, the emulsion is transferred to spray drying at temperature about 170°C at inlet and about 90°C at outlet. There are obtained 36 kg of the health-giving foodstuff according to the invention.

What is claimed is:

1. A health-giving foodstuff containing ethyl esters of fatty acids of linseed oil, characterised in that it is constituted of microcapsules in a form of powder, which contains, in a protein-carbohydrate matrix, a nutraceutical with bioactive ethyl esters of acids ALA (α-Linolenic acid) and LA (Linoleic acid) in a form of drops of diameter less than 2 μm, with not more than 4 percent by weight addition of ethanol based on at least 99,8% anhydrous pharmaceutical ethanol, wherein in the protein-carbohydrate matrix as proteins there are used milk proteins concentrates with decreased lactose concentration, containing minimum 30 percent by weight of proteins and/or plant proteins concentrates, wherein in the protein-carbohydrate matrix as carbohydrate there is used low saccharification maltodextrin with DE (Dextrose Equivalent) index not higher than 13.

2. The foodstuff according to claim 1, characterised in that the microcapsules diameter is 20 - 270 μm.

3. The foodstuff according to claim 1, characterised in that the protein-carbohydrate matrix contains minimal amount up to 5 percent by weight flavouring-colouring additives, vitamins and bio-elements.

4. A method for obtaining a health-giving foodstuff containing ethyl esters of fatty acids of linseed oil, by mixing of ingredients, their homogenisation, drying, characterised in that after obtaining a liquid protein-carbohydrate matrix, a nutraceutical containing bioactive ethyl esters of acids ALA (α-Linolenic acid) and LA (Linoleic acid) is introduced into it, followed by carrying out a dispergation of the ester phase by mechanical agitation until a stable form of emulsion is obtained, which is then treated with two-steps and two-stages pressure homogenisation: at pressure of 20 MPa - 25MPa in a first step of a first stage and 4 MPa - 5MPa in a second step of the first stage at a temperature of 50-70°C, and at pressure of 30 MPa - 60MPa at a temperature of 40-70°C in a first step of a second stage and at pressure of 10 MPa - 15 MPa at a temperature of 50-70°C in a second step of the second stage, whilst homogenisation during the first stage is carried out in a process coupled with thermal

processing of the emulsion, which is then spray dried in atmosphere at a temperature 160-190°C in an inlet of a drying cabinet to produce a powder and the powder is dispensed in a neutral gas atmosphere.

5. The method according to claim 4, characterised in that after homogenisation of the first stage and before homogenisation of the second stage, the emulsion is put aside for 6 hours, and after that is warmed up to 50 - 70°C.

6. The method according to claim 4, characterised in that a continuous phase of the emulsion is obtained by dissolving in water of temperature 30°C the matrix components, that is proteins and polysaccharides, followed by protein hydration and the nutraceutical is introduced after hydration of the components.

7. The method according to claim 4 or 6, characterised in that protein hydration is carried out at temperature 25-35°C for 4 hours.

8. The method according to claim 4, characterised in that during thermal processing the stable emulsion is warmed up to temperature 50 - 65°C, pasteurised and cooled down to 10°C.

9. The method according to claim 4, characterised in that during storage and dispensing of the health-giving foodstuff is carried out in nitrogen as a neutral gas atmosphere.

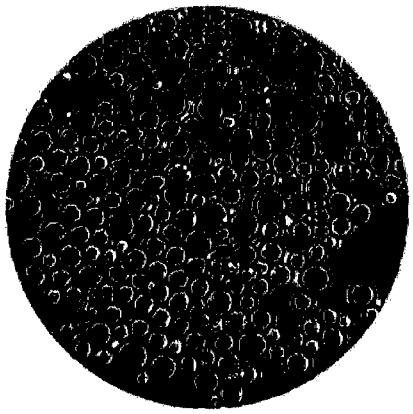


Fig. 1

Emulsion of ethyl esters LL after repeated two-step pressure homogenization (microcapsules are in the liquid form). Mass composition: - water 64,8%, dry mass 35,2% therein: protein MPC75 15,9%, maltodextrin DE 7,3%, LeenLife esters 12,0%. Ester drops form a stable emulsion without tendency to coalescence, in spite of predisposition to flocculation. Diameter of the ester drops does not exceed 2 µm. The picture was taken from an optical microscope under magnification of 40x

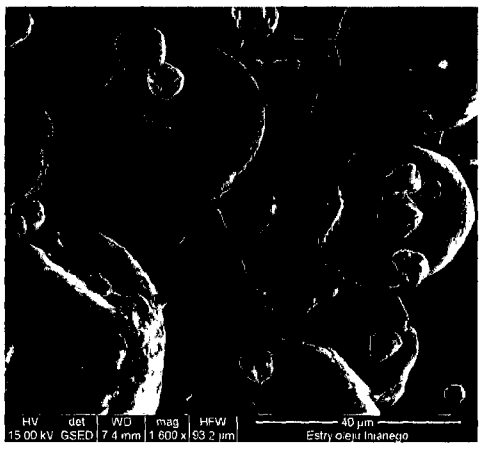


Fig. 2

Microcapsules in the form of powder (32% protein, 33% esters LL, 30% maltodextrin, 3% water) after spray drying - particle size 20 – 270 µm. Avarage particle size d_{32} = 162 µm The figure was taken with an electron microscope at magnification 1600x (scaning microscop Quanta 200, FEI Company).