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<p>(57) Abstract</p> <p>A n-3, n-6 and n-9 unsaturated fatty acid-containing edible product comprising a marine animal ingredient and an oil-in-water emulsion and containing at least 1 wt% of C20:5 and C22:6 n-3 polyunsaturated fatty acids (PUFAs), and a process of preparing the product. The product provides a recommended daily dosage of n-3 PUFAs of 1-4 g in an amount of 40-150 g.</p>		

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AN EDIBLE PRODUCT AND PROCESS OF PREPARING SAME

FIELD OF INVENTION

The present invention relates to an edible product containing n-3, n-6 and n-9 unsaturated fatty acids, comprising a marine animal ingredient and an oil-in-water emulsion which product contains at least 1 wt% of C20:5 and C22:6 n-3 polyunsaturated fatty acids, and a process for preparing the product.

TECHNICAL BACKGROUND

10 The group of fatty acids comprises saturated, monounsaturated and polyunsaturated fatty acids. The term "unsaturated" indicates that the fatty acid contains at least one double bond between carbon atoms. Fatty acids are generally classified according to (1) the length of the carbon chain, (2) 15 the number of double bonds and (3) the position of the last double bond in relation to the methyl terminal of the molecule. As an example, the term C18:2 n-6 (linoleic acid) designates a fatty acid with 18 carbon atoms in the chain and comprising two double bonds of which the first from the 20 methyl end of the fatty acid is at the sixth carbon atom.

Humans are unable to synthesize fatty acids with double bonds more distal from the carboxyl end of the fatty acid than the ninth carbon atom. Thus, n-3 and n-6 unsaturated fatty acids are dietary essential fatty acids which must be 25 supplied in the diet in amounts which are sufficient to maintain normal body functions.

The n-3 polyunsaturated fatty acids (PUFAs) are one important dietary class of polyunsaturated fatty acids of which α -linolenic acid (C18:3 n-3) is the parent compound. α -Linolenic acid is present in plant oils such as linseed, 30 rapeseed and soybean oil. However, marine phytoplankton and

zooplankton are rich sources of longer n-3 polyunsaturated fatty acids and are the source of the abundant C20:5 n-3 eicosapentaenoic (EPA) and C22:6 n-3 docosahexanoic (DHA) acids in marine animals.

- 5 Accordingly, marine animal products are significant dietary sources of lipids containing long chain n-3 polyunsaturated fatty acids, in particular C20:5 n-3 and C22:6 n-3. In marine lipids such long chain PUFAs typically constitute 20-30 wt% of the total fatty acid content.
- 10 n-6 Polyunsaturated fatty acids of which linoleic acid (C18:2 n-6) is the parent compound are the predominant unsaturated fatty acids in many plant oils including safflower oil, corn oil, grape kernel oil, cottonseed oil and sunflower seed oil.
- 15 Oleic acid (C18:1 n-9) is the parent compound for the class of n-9 unsaturated fatty acids which are present in high amounts in animal fat and in certain plant oils/fats such as olive oil and rape seed oil.

It is known that a high dietary intake of saturated fatty acids results in increases of both total serum cholesterol and low-density-lipoprotein (LDL) cholesterol, two important risk factors for development of human atherosclerosis. Recent research has indicated that the replacement of dietary saturated fatty acid by monounsaturated or polyunsaturated fatty acids has significant atherosclerosis risk reducing effects on the composition of blood lipids.

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Thus, monounsaturated fatty acids such as oleic acid (C18:1 n-9) reduce LDL cholesterol without changing high-density-lipoprotein (HDL) cholesterol. The subsequent reduction of the LDL/HDL cholesterol ratio is associated with a reduced risk for atherosclerosis.

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Intake of the n-6 polyunsaturated fatty acids also results in a reduction of total cholesterol and LDL cholesterol. In addition such PUFAs may contribute to a lower risk for thrombosis.

- 5 The long-chain polyunsaturated n-3 fatty acids from marine sources reduce serum triglycerides and very-low-density-lipoprotein, two other atherosclerosis risk factors, whereas the concentration of HDL cholesterol is increased and LDL cholesterol is unchanged or slightly increased. Furthermore, blood platelets, endothelial cells, and perhaps other factors involved in thrombus formation may be affected in an antithrombotic direction by the n-3 long-chain PUFAs.

Furthermore, recent research results have indicated that n-3 PUFAs affect the function of the white blood cells resulting in a certain inhibitory effect on the inflammatory response of the body. This effect may be beneficial in humans suffering from chronic polyarthritis or psoriasis. Since processes associated with the inflammatory response are also involved in the forming of atherosclerotic plaques, n-3 fatty acids may also have an inhibitory effect on such plaque formation. Finally, it has also been found that replacement of saturated fatty acids by unsaturated fatty acids tends to lower the blood pressure.

- 25 From the above, it is obvious that important health improving effects can be obtained by adjusting the fatty acid composition of the daily diet in the direction of higher contents of unsaturated fatty acids in place of saturated fatty acids. Whereas diets in most countries may have a dietary sufficient content of n-6 fatty acids, dietary insufficient amounts of the n-3 and/or n-9 unsaturated fatty acids may occur in many diets. It may, however, be difficult, if not impossible for the common consumer not having special knowledge of the chemical composition of food products and of recommended daily intakes of the

different classes of unsaturated fatty acids, to select a diet which secures an optimal intake of the beneficial unsaturated fatty acids.

5 Recently, several products have been developed which contain n-3 PUFAs in the form of marine oils in dosages which will provide the recommended daily dosage of 2-4 g of these fatty acids. A majority of such products are in the form of air-tight capsules.

10 It is also known to supplement various food products such as margarine and bakery products with marine oils. However, such n-3 fatty acid enriched food products do not provide a recommended daily dosage of n-3 PUFAs unless large quantities of the food products are consumed regularly.

15 One obvious way of providing a high dietary intake of n-3 PUFAs would be to consume high quantities of fatty fish like salmon or mackerel on a daily basis. However, this approach would require a daily consumption of fatty fish in the order of 100-200 g. It is known to prepare products containing fatty fish in a conventional oil-in-water emul-
20 sion dressing or mayonnaise. Examples of such products include herring salads in a mayonnaise-type dressing and cooked mackerel in mayonnaise. Such products may contain n-9 and/or n-6 fatty acids in amounts which are typically in the range of 5-15 g/100 g. However, the content of n-3
25 PUFAs is in the range of 0.4-0.8 g/100 g. Accordingly, it is not feasible to provide a recommended daily dosage of n-3 PUFAs with such known products. It should also be mentioned that these known products are not generally
30 manufactured and packaged under oxygen conditions which prevent oxidation and rancidity development of the polyunsaturated fatty acids.

There is clearly a need for palatable food products which in dietary acceptable amounts provide daily dietetically effective dosages of n-3 polyunsaturated fatty acids. By

providing in the same food product a mixture of such n-3 polyunsaturated fatty acids and other classes of unsaturated fatty acids having additive health improving effects, in particular n-9 fatty acids, consumers are offered an easy-to-grasp opportunity to improve their diet.

The present invention provides novel edible products containing in a package unit a recommended daily dosage of n-3 polyunsaturated fatty acids and a dietetically effective amount of n-9 unsaturated fatty acids.

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SUMMARY OF THE INVENTION

In a first aspect, the present invention relates to an edible product containing a mixture of n-3, n-6 and n-9 unsaturated fatty acids comprising (a) 10-90 wt% of a marine animal ingredient and (b) 10-90 wt% of an oil-in-water emulsion comprising an oily phase which is in the range of 20-80 wt%, calculated on the emulsion, said edible product having a content of C20:5 and C22:6 n-3 polyunsaturated fatty acids which is at least 1 wt%. The product may further comprise 0.1-25 wt% of non-liquid vegetable and/or fruit ingredients and it may conveniently be in the form of portions contained in a package material preferably having a low oxygen penetration coefficient.

In an other aspect, the invention provides a process for preparing the edible product containing a mixture of n-3, n-6 and n-9 unsaturated fatty acids and having a content of C20:5/C22:6 n-3 polyunsaturated fatty acids being at least 1 wt%, said process comprising the following steps:

(i) subjecting demineralized water to a sparging treatment with an inert gas,

(ii) subjecting one or more edible oils to a sparging treatment with an inert gas,

(iii) mixing under emulsifying conditions in an atmosphere of an inert gas, water resulting from (i), at least one edible oil resulting from (ii) and an emulsifying agent to obtain an oil-in-water emulsion having an oily phase being
5 in the range of 20-80 wt%,

(iv) mixing in an atmosphere of an inert gas the emulsion of step (iii) with a marine animal ingredient, and optionally

10 (v) adding to the mixture resulting from step (iv) one or more non-liquid vegetable and/or fruit ingredients, to obtain the edible product wherein the proportion of the marine animal product is in the range of 10-90 wt%, the proportion of the oil-in-water emulsion in the range of
15 20-80 wt% and the proportion of the non-liquid vegetable and/or fruit ingredient, when present being in the range of 0.1-25 wt%, and

(vi) distributing under an atmosphere of an inert gas the edible product into portions contained in a package material.
20 al.

DETAILED DISCLOSURE OF THE INVENTION

As previously defined, the edible product according to the invention comprises 10-90 wt% of a marine animal ingredient
25 and 10-90 wt% of an oil-in-water emulsion. In the present context the term "marine animal" include any edible aquatic animal such as salt-water fish, fresh water fish, aquatic mammals including whales and seals; shellfish including shelled mollusks such as clams and crustaceans such as
30 lobsters, shrimps, crabs and barnacles; and Cephalopoda spp such as octopus spp and squids. The product according to the invention may contain one marine animal ingredient or a mixture of such ingredients.

The marine animal ingredient may conveniently be a cooked ingredient e.g. in the form of tinned products which have been subjected to a pressure cooking process. In such cooked ingredients, the proteins are coagulated as a result of the heat treatment.

In other useful embodiments, the marine animal ingredient is a raw ingredient which has been subjected to a conventional pickling treatment. Typically, such a treatment is carried out by storing a marine animal or parts thereof in a brine for several weeks or months. Alternatively, the marine animal ingredient is pickled by keeping it in a marinade essentially comprising vinegar, salt and flavouring agents. Due to the high acid content of the marinade, such a treatment will result in at least a partial coagulation of the ingredient proteins. Typically, commercial acid-pickled marine animal products such as pickled herring has a salt content in the range of 3-5 wt% and a pH in the range of 3-5. The marine animal ingredient may also be a raw or pickled ingredient which has been subjected to a smokecuring treatment.

In interesting embodiments of the invention, the marine animal ingredient is a fish ingredient selected from fish meat, fish liver and fish roe. In the present context, a useful fish ingredient may be an ingredient derived from fish selected from the group consisting of anchovy, white fish, dogfish, eel, herring, mackerel, menhaden, sardine, squid, tuna, salmon and trout.

Particularly useful fish ingredients are derived from fish species having a high content of long-chained polyunsaturated fatty acids including C20:5 and C22:6 n-3 fatty acids. Accordingly, the fish ingredient may advantageously have a content of such n-3 unsaturated fatty acids which is at least 0.5 wt%, preferably at least 1.0 wt% and most preferably at least 1.5 wt%. Examples of fish species having

in their flesh such a high content of the C20:5 and C22:6 n-3 polyunsaturated fatty acids include herrings, anchovies, mackerel, menhaden and sardines. In general, roe and the liver of fish, even from fish with a low content of the long-chained n-3 fatty acids in the flesh, has a high content of these fatty acids. Accordingly, fish roe such as cod roe and fish liver oil are useful sources of C20:5 and C22:6 n-3 polyunsaturated fatty acids in the products according to the invention.

10 The above-defined marine animal ingredient may be in the form of an ingredient cut into pieces of a suitable form and size. Thus, the pieces may e.g. be essentially cubic or shredded. Conveniently, the pieces have a largest edge size which is in the range of 1-50 mm, preferably in the range of 5-40 mm and more preferably in the range of 10-20 mm. In other useful embodiments, the marine animal ingredient is in the form of flakes or slices of cooked meat or in the form of a comminuted or mashed ingredient which has a particle size (largest diameter) e.g. being in the range of 0.1-5 mm such as in the range of 0.2-2 mm.

The marine animal ingredient may be distributed substantially evenly in the oil-in-water emulsion of the product, although it will be understood that an initially evenly distributed ingredient as a result of the gravity of the pieces or particles may tend to become dislocated downward during storage of the product. The extent of this dislocation will i.a. depend on the viscosity of the emulsion. If desirable, a product in which the storage dislocation of the marine animal ingredient pieces or particles is controlled may be prepared by using an emulsion having a high viscosity. Products in which the marine animal ingredient remains essentially evenly distributed may be prepared by using a finely divided ingredient optionally mixed with an oil-in-water emulsion having a high viscosity.

In other embodiments of the invention, the marine animal ingredient and the oil-in water emulsion are present in the edible product as separate parts e.g. as essentially separated layers. Conveniently, the oil-in-water emulsion
5 may be poured on top of the marine animal ingredient. The separation of the ingredients may also be achieved by distributing the ingredients separately into a multiple-compartment container which may conveniently be provided with an easily breakable partition wall between the com-
10 partments.

In preferred embodiments, the product according to the invention has a content of marine animal ingredient which is in the range of 20-80 wt%. More preferably, the content is in the range of 30-70 wt%, even more preferably in the
15 range of 40-60 wt%. In particularly preferred embodiments, the content of the marine animal ingredient is about 50 wt%.

As defined above, the edible product according to the invention comprises 10-90 wt% of an oil-in-water emulsion.
20 In other embodiments of the invention the content is preferably in the range of 30-60 wt% and more preferably in the range of 35-50.

In accordance with the invention, the oil-in-water emulsion comprises 20-80 wt% of a dispersed oily phase. As used
25 herein, the term "edible oil" includes natural or synthesized lipid substances consisting essentially of triglycerides which preferably have a melting point in the temperature range of 0-30°C. Such substances include as examples vegetable oils such as olive oil, rape seed oil, grape
30 kernel oil, maize oil, soybean oil, sunflower seed oil, corn oil or coconut oil and marine animal oils such as fish oils and oils from marine mammals. The oils may be partially hydrogenated, fractionated, interesterified or otherwise modified. In the present context, useful oils
35 include lipid substances having properties similar to those

of triglycerides, which substances may be indigestible such as polyol fatty acid polyesters.

In other preferred embodiments, the oily phase comprises a mixture of two or more edible oils. The selection of the composition of edible oils is primarily based on the consideration that the product should have a total content of n-3, n-6 and n-9 polyunsaturated fatty acids which is in the range of 5-30 wt%, preferably in the range of 10-20 wt% such as in the range of 14-19 wt%, the content of long-chained C20:5 and C22:6 n-3 polyunsaturated fatty acids being at least 1 wt%, such as at least 1.5 wt% or more preferably at least 2.0 wt%. Accordingly, it is preferred that at least one oil is a marine animal oil which provides a high content of the C20:5 and C22:6 n-3 polyunsaturated fatty acids.

Advantageously, the oily phase is a mixture of at least three edible oils of which at least one is an oil derived from a marine animal. Such marine animal oils are included as a primary source of C20:5 and C22:6 n-3 polyunsaturated fatty acids. Useful marine animal oils include fish oils which are obtained from fish meat, roe and liver of the fish species mentioned above. Typically, a commercial fish oil product will be a mixture of oils from different species and/or from different parts of fish. The content of n-3 PUFAs in commercial fish oils is typically in the range of 10-50 wt% such as in the range of 20-30 wt% whereof typically 80-90 wt% are C20:5 and C22:6 n-3 polyunsaturated fatty acids.

Suitably, a marine animal oil should have a bland non-fishy taste. Commercial marine oils are available which have been subjected to a refining process to remove substances conferring the fishy taste. It is preferred to use such refined marine oils.

Due to their high content of PUFAs, marine oils are particularly vulnerable to rancidity deterioration resulting from oxidation processes resulting either from the action of oxygen from the atmosphere or from the action of oxygen dissolved in the oil product itself.

Accordingly, marine oils which are useful in the present invention have a low degree of rancidity. In the fish oil industry the degree of rancidity is typically measured as the anisidine value (Deutsche Einheitsmethoden, 1977 C-VI 6 e (77)). Suitably, oils used herein should have an anisidine value less than 10 and preferably less than 5.

It may be advantageous to use marine oils which contain an antioxidant. Suitable antioxidants include naturally occurring antioxidants such as tocopherol and conventional lipid-soluble antioxidants including as examples ascorbyl palmitate, propyl gallate and citric acid.

In one useful embodiment, the oily phase comprises at least one edible oil having a content of n-9 polyunsaturated fatty acids which is at least 50 wt%. Examples of such oils are olive oil, which typically contains about 50-90 wt% of n-9 PUFAs and rape seed oil in which the content of n-9 PUFAs is about 55 wt%. The predominant n-9 PUFA in these vegetable oils is C18:1. Olive oil may be used in the form of extra virgin olive oil, virgin olive oil or in the form of standard olive oil which is partially refined olive oil product from which i.a. flavouring substances have been removed.

In a further useful embodiment, the oily phase comprises at least one edible oil containing at least 50 wt% of n-6 PUFAs. Such oils include as an example grape kernel oil of which about 50-90 wt% is C18:2 n-6 fatty acids.

In one preferred embodiment, the oily phase of the oil-in-water emulsion is a mixture of a marine oil and two dif-

ferent vegetable oils selected from the group consisting of olive oil, grape kernel oil, rape seed oil, maize oil, sunflower seed oil and soybean oil including as one useful example a particular embodiment in which the oily phase contains marine oil, olive oil and grape kernel oil in a ratio which is about 3:5:2.

In a further preferred embodiment, the content of the oily phase in the emulsion ingredient is in the range of 30-50.

The oil-in-water emulsion comprises 20-80 wt% of an aqueous phase. The water of this phase is preferably demineralized water with a content of oxidizing (prooxidatively active) metals such as copper and iron being so low that it does not cause oxidation of fatty acid double bonds. The aqueous phase incorporates water soluble ingredients conventionally used in edible oil-in-water emulsions. Such ingredients include stabilizing and thickening agents such as guar gum, carrageenans, alginates, pectins, cellulose derivatives and gelatine; salt; preservatives including as examples alkali metal sorbates and benzoates; sweetening agents such as glucose, fructose, saccharose, glucose syrup and muscuvado; flavouring agents such as mustard; acidifying agents such as vinegar or citric acid; antioxidants including citric acid.

The emulsion further comprises an emulsifying agent. Any conventionally used emulsifier can be used. Such emulsifying agents include egg yolk, egg yolk lecithin, vegetable lecithins such as soybean lecithin, proteins as e.g. milk proteins, fatty acid derivatives such as glycerol partial fatty acid esters including as examples glycerol monostearate or glycerol distearate or mixtures of such emulsifiers.

The product according to the invention may preferably further contain 0.1-25 wt% of non-liquid vegetable and/or fruit ingredients which are added in order to confer a certain desired taste, flavour and consistency. Such ingre-

dients may e.g. be vegetables divided into suitable pieces such as pieces having a largest edge length in the range of 1-10 mm. In preferred embodiments the vegetables are in the form of pickled vegetables which prior to the pickling treatment may have been subjected to a heat treatment. Examples of useful vegetables are carrots, celery, celeriac, paprika, onions, cucumber, tomatoes and bamboo shoots. Examples of fruits which are useful in products according to the invention include mango, apricots, apples and pears and citrus fruits.

Useful product recipes may also include aromatic herbs in fresh or blanched state or as dried herbs, e.g. tarragon, dill, parsley, oregano and chives.

As mentioned above, the recommended daily intake of n-3 PUFAs is in the range of 1-4 g. Accordingly, the product according to the invention is preferably provided in the form of a portion contained in a package material which contains an amount of n-3 PUFAs corresponding to the recommended daily intake. The size of a product portion providing the above amount of n-3 PUFAs depends on the amounts of these fatty acids in the marine animal ingredient and in the emulsion. By selecting a marine animal ingredient with a high content of fat and/or using a high proportion of marine oil in the emulsion the portion can be made as small as it is possible. It is generally preferred that the portion has a size in the range of 40-150 g, e.g. in the range of 50-100 g such as about 60 g.

As discussed hereinbefore, PUFAs are prone to oxidation and rancidity deterioration. Such deterioration processes lead to rancid and fishy taste and to a reduction in the health improving effects of the fatty acids. Accordingly, the product according to the invention has a content of oxygen which preferably is at the most 1.0 cm³/100 g. More preferably, the oxygen content is at the most 0.75 cm³/100 g, even more preferably at the most 0.5 cm³/100 g, most pre-

ferably at the most $0.25 \text{ cm}^3/100 \text{ g}$ and in particular at the most $0.10 \text{ cm}^3/100 \text{ g}$.

In order to provide the present products with such a low content of oxygen it is necessary to select product raw materials with the lowest possible oxygen content and select a process of preparing which substantially does not increase the total oxygen content. It is, however, also commercially required that the products are stable during storage in the product distribution channels, the term "stable" being used in the present context to indicate that the unsaturated fatty acids of the product are not oxidized to an extent where undesired rancidity off-flavours become sensorically recognizable.

The rancidity of the products is typically measured as the thiobarbiturate (TBA) value which is an indication of the content of the oxidation products malic dialdehyde and glycoaldehyde (Wyncke, 1975, Fette, Seifen, Anstrichmittel, 77). Preferably, the products should have a TBA value as defined above which is less than $0.02 \text{ } \mu\text{mol/g}$, more preferably less than $0.01 \text{ } \mu\text{mol/g}$ and in particular less than $0.005 \text{ } \mu\text{mol/g}$ even after storage at $5-10^\circ\text{C}$ such as at 8°C for at least 6 weeks, preferably for at least 8 weeks.

In order to obtain the above-defined stability, the product according to the invention is advantageously packaged in a material which is essentially oxygen-tight, such materials including tin foil, aluminium foil, glass, and plastic packaging materials comprising at least one polymer having an oxygen penetration coefficient which at 23°C is at the most $2.0 \text{ cm}^3/0.025 \text{ mm/m}^2/24\text{h/atm}$, preferably at the most $1.0 \text{ cm}^3/0.025 \text{ mm/m}^2/24\text{h/atm}$ and most preferably at the most $0.5 \text{ cm}^3/0.025 \text{ mm/m}^2/24\text{h/atm}$. Examples of suitable plastic materials comprising an oxygen barrier polymer are laminated materials of e.g. polypropylene, polyethylene and/or polystyrene. In such laminated materials suitable oxygen barrier materials are e.g. EVOH and PVDC copolymers.

In useful embodiments of the invention, the weight ratio between C20:5/C22:6 n-3 polyunsaturated fatty acids and n-9 polyunsaturated fatty acids of the product is in the range of 1:9 - 1:1, preferably in the range of 1:6.7 - 1:2.7 and
5 more preferably in the range of 1:4 - 1:3.

In other useful embodiments, at least 25 wt% such as at least 33 wt% or at least 50 wt% of the total content of C20:5/C22:6 n-3 polyunsaturated fatty acids in the product according to the invention is derived from the marine
10 animal ingredient.

Furthermore, it may be advantageous to include in the oil-in-water emulsion a proportion of a marine oil as defined above which is at least 20 wt% such as at least 30 wt%. In
15 certain embodiments it may be preferred to use an even higher proportion, e.g. at least 40 wt% such as at least 50 wt%.

As mentioned above, the present invention relates in one aspect to a process for preparing an edible product as
20 defined above. The process may be carried by using conventionally used mixing and packaging equipment.

The present process includes measures to reduce the amount of dissolved oxygen in the resulting products and to maintain this amount at a level where a suitable product stability as also defined above (shelf life) under conventional
25 storage conditions is achieved. Accordingly, the process includes as initial steps that the liquid ingredients including demineralized water and oils are subjected separately or as mixtures to a sparging treatment with an
30 inert gas to reduce the amount of dissolved oxygen in the ingredients to a level which is at the most 0.2 mg/L and preferably at the most 0.1 mg/L.

In the present context, the term "inert gas" is used to define a gas which does not react with the double bonds of

the unsaturated fatty acids. A convenient inert gas is nitrogen and accordingly, a suitable sparging treatment comprises injecting nitrogen bobbles into the liquids ingredients until the amount of dissolved oxygen herein was
5 reduced to at the most 0.2 mg/L. Although nitrogen is a preferred gas, any other inert gas including CO₂ and hydrogen can be used in the sparging treatment.

As previously defined, further steps of the process includes the step of preparing an oil-in-water emulsion as
10 defined above and a step of mixing the obtained emulsion with the marine animal ingredient in an atmosphere of an inert gas. This gas atmosphere may be provided by placing the mixing equipment in a chamber or a room filled with the inert gas or by constant flushing of the equipment with the
15 inert gas. Optionally, a further step is carried out in which one or more non-liquid vegetable and/or fruit ingredients is/are added to the emulsion/marine animal ingredient mixture. If carried out, this step also takes place in an inert gas atmosphere.

20 As a final step, the process comprises distributing under an atmosphere of an inert gas, the edible product into portions as defined above and contained in a package material as also defined hereinbefore.

The invention is illustrated in the following examples:

EXAMPLE 1

Preparation of pickled herring salad containing vegetables

A salad product containing pickled herring and a mixture of vegetables were prepared according to the following recipe:

5	Demineralized water	10.73 wt%
	Guar gum	0.06 wt%
	Sodium alginate	0.10 wt%
	Fructose	1.63 wt%
	Glucose syrup	1.37 wt%
10	Sodium benzoate	0.01 wt%
	Potassium sorbate	0.01 wt%
	Sodium caseinate	0.20 wt%
	Fish oil	3.90 wt%
	Olive oil	6.34 wt%
15	Grape kernel oil	2.68 wt%
	Grindox™ 117 ¹⁾	0.01 wt%
	Citric acid	0.01 wt%
	Salt	0.59 wt%
	Vinegar	3.66 wt%
20	Mustard	2.05 wt%
	Nutmeg	0.09 wt%
	Vegetable extract	0.34 wt%
	Lemon oil	0.01 wt%
	Chive	1.32 wt%
25	Vegetable mixture ²⁾	14.92 wt%
	Pickled herring ³⁾	50.00 wt%

1) Antioxidant composition containing 7.5 wt% ascorbyl palmitate, 17.5 wt% propylgallate, 10 wt% citric acid, emulsifying agent and propylene glycol.

2) About equal amounts of pickled carrots (pieces of about 2 x 2 x 10 mm), celery and celeriae (pieces of about 5 x 5 x 5 mm).

3) Cut into pieces of about 5 x 30-40 mm.

5 Initially, the demineralized water, fish oil, olive oil and grape kernel oil were subjected to a nitrogen sparging treatment by injecting nitrogen bobbles into these liquids until the amount of dissolved oxygen herein was reduced to at the most 0.2 cm³/L.

10 The oils were mixed and the antioxidant composition dissolved in the mixture followed by suspending the sodium caseinate in the resulting mixture.

An oil-in-water emulsion dressing was prepared by means of a KORUMA™ emulsion turbine. The demineralized water was
15 poured into the mixing vessel of the turbine and all dry ingredients except salt and sodium caseinate (guar gum, sodium alginate, fructose, glucose syrup, sodium benzoate and potassium sorbate) were added and dissolved by mixing for about 2 minutes under vacuum and flushing with nitrogen
20 to obtain an aqueous phase. Subsequently, the oily phase containing the antioxidant composition and the caseinate were added slowly to the aqueous phase and mixing was continued under vacuum and nitrogen flushing until the two phases were homogeneously emulsified. Finally, the vinegar,
25 salt, mustard and citric acid were added to the emulsion and mixing continued until these ingredients were distributed evenly into the emulsion to obtain a dressing.

Herring fillets pickled in vinegar, salt and spices were cut into pieces of about 5 x 30-40 mm. The pickled herring,
30 the vegetable mixture and chive were mixed into the dressing together by stirring under nitrogen atmosphere.

The resulting pickled herring salad containing vegetables were distributed in 150 g portions into aluminium foil bags which were evacuated after filling and subsequently flushed with nitrogen to obtain a content of oxygen of

5 0.85 cm³/150 g of product. Alternatively, the product was packaged under nitrogen atmosphere in suitable containers of laminated plastic materials such as beakers made from polystyrene, polypropylene, polyethylene or combinations hereof and comprising a EVOH oxygen barrier of at least 30

10 μm. The filled containers were flushed with nitrogen prior to being sealed with an aluminium foil lid to obtain a content of oxygen in the head space of at the most

0.1 vol%.

Based upon typical fatty acid compositions of the oils used

15 in the present fish salad product it was calculated that the product per 100 g had a content of n-9 unsaturated fatty acids in the range of 7.8-9.3 g, a content of n-6 PUFAs in the range of 2.8-3.7 g, a total content of n-3 PUFAs in the range of 2.3-2.7 g of which about 90% were the

20 long chain marine EPA and DHA.

EXAMPLE 2

Preparation of herring salad with aromatic plants

A fish salad product containing pickled herring and a mixture of aromatic plants were prepared according to the

25 following recipe:

	Demineralized water	17.52 wt%
	Guar gum	0.07 wt%
	Sodium alginate	0.11 wt%
	Glucose	0.13 wt%
5	Fructose	1.89 wt%
	Glucose syrup	1.55 wt%
	Sodium benzoate	0.01 wt%
	Sodium caseinate	0.27 wt%
	Fish oil	5.39 wt%
10	Olive oil ³⁾	12.47 wt%
	Grindox™ 117	0.01 wt%
	Grindox™ 1030 ¹⁾	0.01 wt%
	Citric acid	0.02 wt%
	Salt	0.61 wt%
15	Tarragon vinegar	1.33 wt%
	Vinegar	1.38 wt%
	Mustard	1.35 wt%
	White pepper	0.02 wt%
	Vegetable extract	0.47 wt%
20	Dill oil	0.01 wt%
	Chives	2.02 wt%
	Parsley	0.67 wt%
	Dill	1.38 wt%
	Pickled herring ²⁾	50.00 wt%

25 1) Antioxidant composition containing 20.0 wt% ascorbyl palmitate, 14.0 wt% tocopherol, emulsifying agent and propylene glycol.

2) Pickled herring fillets cut into pieces of about 5 x 30-40 mm.

30 3) A mixture of extra virgin olive oil and refined olive oil.

The salad product was prepared essentially according to the process of Example 1.

The calculated fatty acid composition of this product were essentially the same as that of the product of Example 1.

EXAMPLE 3

Preparation of "Bombay herring salad"

5 This salad product was prepared according to the following recipe:

	Demineralized water	12.79 wt%
	Guar gum	0.07 wt%
	Sodium alginate	0.10 wt%
10	Fructose	1.49 wt%
	Glucose syrup	1.18 wt%
	Sodium benzoate	0.01 wt%
	Potassium sorbate	0.01 wt%
	Sodium caseinate	0.19 wt%
15	Fish oil	4.02 wt%
	Olive oil	6.39 wt%
	Grape kernel oil	2.60 wt%
	Grindox™ 117	0.01 wt%
	Grindox™ 1030	0.01 wt%
20	Citric acid	0.01 wt%
	Salt	0.24 wt%
	Vinegar	2.60 wt%
	Curry	1.75 wt%
	Chili paste	0.71 wt%
25	Vegetable mixture ¹⁾	15.82 wt%
	Pickled herring ²⁾	50.00 wt%

1) Mixture of pickled apricot (33.33 wt%), sweet mango chutney (16.13 wt%), pickled red paprika (33.33 wt%) and pickled onions (17.20 wt%).

2) Pickled herring fillets cut into pieces of about 5 x 30-40 mm.

The salad product was prepared essentially according to the process of Example 1.

5 EXAMPLE 4

Preparation of mustard dressing herring salad

This salad product was prepared essentially according to the process as defined in Example 1 based on the following recipe:

10	Demineralized water	10.37 wt%
	Glucose	0.10 wt%
	Fructose	1.45 wt%
	Muscovado	2.80 wt%
	Glucose syrup	1.24 wt%
15	Sodium caseinate	0.47 wt%
	Fish oil	5.71 wt%
	Olive oil	9.34 wt%
	Grape kernel oil	3.63 wt%
	Grindox™ 117	0.01 wt%
20	Grindox™ 1030	0.01 wt%
	Citric acid	0.02 wt%
	Vinegar	3.89 wt%
	Mustard	10.37 wt%
	Oil of anise	0.03 wt%
25	Dill	0.31 wt%
	Pernod	0.26 wt%
	Pickled herring ¹⁾	50.00 wt%

1) Pickled herring fillets cut into pieces of about 5 x 30-40 mm.

CLAIMS

1. An edible product containing a mixture of n-3, n-6 and n-9 unsaturated fatty acids comprising

(a) 10-90 wt% of an marine animal ingredient and

5 (b) 10-90 wt% of an oil-in-water emulsion comprising an oily phase which is in the range of 20-80 wt%, calculated on the emulsion, an aqueous phase and an emulsifying agent,

said edible product having a content of C20:5 and C22:6 n-3
10 polyunsaturated fatty acids which is at least 1 wt%.

2. A product according to claim 1 wherein the content of oxygen is at the most 1.0 cm³/100 g.

3. A product according to claim 1 or 2 which further comprises 0.1-25 wt% of non-liquid vegetable and/or fruit
15 ingredients.

4. A product according to claim 2 or 3 which is in the form of a portion contained in a package material.

5. A product according to claim 4 wherein the portion has a size which is in the range of 40-150 g.

20 6. A product according to claim 5 wherein the portion size is in the range of 50-100 g.

7. A product according to any of claims 4-6 wherein the portion has a content of n-3 unsaturated fatty acids which is in the range of 1-4 g.

25 8. A product according to claim 2 wherein the content of oxygen/100 g is at the most 0.75 cm³, preferably at the most 0.5 cm³ and in particular at the most 0.25 cm³.

9. A product according to claim 4 wherein the package material comprises a polymer having an oxygen penetration which at 23°C is at the most $2.0 \text{ cm}^3/0.025 \text{ mm/m}^2/24\text{h/atm}$, preferably at the most $1.0 \text{ cm}^3/0.025 \text{ mm/m}^2/24\text{h/atm}$ and most
5 preferably at the most $0.5 \text{ cm}^3/0.025 \text{ mm/m}^2/24\text{h/atm}$.
10. A product according to claim 1 or 2 wherein the marine animal ingredient has a content of n-3 unsaturated fatty acids which is at least 1 wt%.
11. A product according to any of preceding claims wherein
10 the content of marine animal ingredient is in the range of 20-80 wt%, preferably in the range of 30-70 wt% and more preferably in the range of 40-60 wt%.
12. A product according to claim 11 wherein the content of marine animal ingredient is about 50 wt%.
- 15 13. A product according to claim 1 or 2 wherein the content of the oil-in-water emulsion is in the range of 20-80 wt%, preferably in the range of 30-60 wt% and more preferably in the range of 35-50 wt%.
- 20 14. A product according to claim 1 or 2 wherein the emulsion comprises an oily phase which is in the range of 30-50 wt%.
15. A product according to claim 1 or 2 wherein the oily phase is a mixture of a two or more edible oils.
- 25 16. A product according to claim 1 or 15 wherein at least one edible oil is a marine oil.
17. A product according to claim 16 which contains olive oil.

18. A product according to claim 17 wherein at least one edible oil has a content of n-6 unsaturated fatty acids which is at least 50 wt% of the total content of fatty acids hereof.
- 5 19. A product according to claim 16 wherein at least one edible oil has a content of n-9 unsaturated fatty acids which is at the least 50 wt% of the total content of fatty acids hereof.
- 10 20. A product according to any of claims 15-19 wherein the oily phase is a mixture of a marine oil and two different vegetable oils selected from the group consisting of olive oil, grape kernel oil, rape seed oil, maize oil, sunflower oil and soy oil.
- 15 21. A product according to claim 20 wherein the oily phase of the emulsion contains marine oil, olive oil and grape kernel oil in a ratio which is about 3:5:2.
22. A product according to claim 3 wherein the content of the non-liquid vegetable and/or fruit ingredients is in the range of 2-20 wt% and preferably in the range of 4-18 wt%.
- 20 23. A product according to any of preceding claims wherein the marine animal ingredient is a fish ingredient selected from fish meat, fish liver and fish roe.
- 25 24. A product according to claim 23 wherein the fish ingredient is derived from fish selected from the group consisting of anchovy, white fish, dogfish, eel, herring, mackerel, menhaden, sardine, squid, tuna, salmon and trout.
- 30 25. A product according to claim 23 wherein the fish ingredient has a total content of C20:5 and C22:6 n-3 unsaturated fatty acids which is at least 0.5 wt%, preferably at least 1.0 wt% and most preferably at least 1.5 wt%.

26. A product according to claim 25 wherein the fish ingredient is herring.
27. A product according to claim 26 wherein the herring is in the form of pickled herring.
- 5 28. A product according to claim 1 or 2 wherein the marine animal ingredient is a crustacean product.
29. A product according to any of preceding claims wherein the marine animal ingredient is in the form of pieces having a largest edge length being in the range of 1-50 mm.
- 10 30. A product according to claim 29 wherein the marine animal ingredient pieces have a largest edge length which is in the range of 5-40 mm and preferably in the range of 10-20 mm.
- 15 31. A product according to any of preceding claims wherein the content of C20:5 and C22:6 n-3 polyunsaturated fatty acids is at least 1.5 wt%, preferably at least 1.75 wt%, more preferably at least 2.0 wt% and in particular at least 2.25 wt%.
- 20 32. A product according to any of preceding claims wherein the marine animal product is a product which has not been subjected to a heat treatment leading to coagulation of the proteins hereof.
- 25 33. A product according to any of preceding claims wherein the weight ratio between C20:5/C22:6 n-3 polyunsaturated fatty acids and n-9 polyunsaturated fatty acids is in the range of 1:9 - 1:1, preferably in the range of 1:6.7 - 1:2.7 and more preferably in the range of 1:4 - 1:3.

34. A product according to any of preceding claims wherein at least 25% of the content of C20:5/C22:6 n-3 polyunsaturated fatty acids is from the marine animal ingredient.

35. A product according to claim 34 wherein at least 33% of
5 the content of C20:5/C22:6 n-3 polyunsaturated fatty acids is from the marine animal ingredient.

36. A product according to claim 35 wherein at least 50% of
10 the content of C20:5/C22:6 n-3 polyunsaturated fatty acids is from the marine animal ingredient.

37. A process for preparing an edible product containing a mixture of n-3, n-6 and n-9 unsaturated fatty acids and having a content of C20:5/C22:6 n-3 polyunsaturated fatty acids being at least 1 wt%, said process comprising the
15 following steps:

(i) subjecting demineralized water to a sparging treatment with an inert gas,

(ii) subjecting one or more edible oils to a sparging treatment with an inert gas,

20 (iii) mixing under emulsifying conditions in an atmosphere of an inert gas, water resulting from (i), at least one edible oil resulting from (ii) and an emulsifying agent to obtain an oil-in-water emulsion having an oily phase being in the range of 20-80 wt%.

25

(iv) mixing in an atmosphere of an inert gas the emulsion of step (iii) with a marine animal ingredient, and optionally

30

(v) adding to the mixture resulting from step (iv) one or more non-liquid vegetable and/or fruit ingredients,

to obtain the edible product wherein the proportion of the marine animal ingredient is in the range of 10-90 wt%, the proportion of the oil-in-water emulsion in the range of 20-80 wt% and the proportion of the non-liquid vegetable and/or fruit ingredient, when present being in the range of 0.1-25 wt%, and

(vi) distributing under an atmosphere of an inert gas the edible product into portions contained in a package material.

10 38. A process according to claim 37 wherein the resulting product has an oxygen content which is at the most 1.0 cm³/100 g.

39. A process according to claim 37 or 38 wherein the portions have a size which is in the range of 40-150 g.

15 40. A process according to claim 39 wherein the portion size is in the range of 50-100 g.

41. A process according to any of claims 39-40 wherein the portion has a content of n-3 unsaturated fatty acids which is in the range of 1-4 g.

20 42. A process according to claim 38 wherein the content of oxygen/100 g is at the most 0.75 cm³, preferably at the most 0.5 cm³ and in particular at the most 0.25 cm³.

43. A process according to claim 37 wherein the package material comprises a polymer having an oxygen penetration which at 23°C is at the most 2.0 cm³/0.025 mm/m²/24h/atm, preferably at the most 1.0 cm³/0.025 mm/m²/24h/atm and most preferably at the most 0.5 cm³/0.025 mm/m²/24h/atm.

44. A process according to claim 37 or 38 wherein the animal marine product has a content of n-3 unsaturated fatty acids which is at least 1 wt%.

45. A process according to any of preceding claims 37-44 wherein the content of animal marine product is in the range of 20-80 wt%, preferably in the range of 30-70 wt% and more preferably in the range of 40-60 wt%.
- 5 46. A process according to claim 45 wherein the content of marine animal ingredient is about 50 wt%.
47. A process according to claim 37 wherein the content of the oil-in-water emulsion is in the range of 20-80 wt%, preferably in the range of 30-60 wt% and more preferably in
10 the range of 35-50 wt%.
48. A process according to claim 37 wherein the emulsion comprises an oily phase which is in the range of 30-50 wt%.
49. A process according to claim 37 wherein the oily phase is a mixture of a two or more edible oils.
- 15 50. A process according to claim 37 or 49 wherein at least one edible oil is a marine oil.
51. A process according to claim 49 wherein one edible oil is olive oil.
52. A process according to claim 49 wherein at least one
20 edible oil has a content of n-6 unsaturated fatty acids which is at least 50 wt% of the total content of fatty acids hereof.
53. A process according to claim 49 wherein at least one
25 edible oil has a content of n-9 unsaturated fatty acids which is at the least 50 wt% of the total content of fatty acids hereof.

54. A process according to any of claims 47-53 wherein the oily phase is a mixture of a marine oil and two different vegetable oils selected from the group consisting of olive oil, grape kernel oil, rape seed oil, maize oil and soy oil.
55. A process according to claim 54 wherein the oily phase of the emulsion contains marine oil, olive oil and grape kernel oil in a ratio which is about 3:5:2.
56. A process according to claim 37 wherein the content of the non-liquid vegetable and/or fruit ingredients is in the range of 2-20 wt% and preferably in the range of 5-18 wt%.
57. A process according to any of preceding claims 37-56 wherein the marine animal ingredient is a fish ingredient selected from fish meat, fish liver and fish roe.
58. A process according to claim 57 wherein the fish ingredient is derived from fish selected from the group consisting of anchovy, cod, dogfish, eel, herring, mackerel, menhaden, sardine, squid, tuna, salmon and trout.
59. A process according to claim 58 wherein the fish ingredient has a content of C20:5 and C22:6 n-3 unsaturated fatty acids which is at least 0.5 wt%, preferably at least 1.0 wt% and most preferably at least 1.5 wt%.
60. A process according to claim 59 wherein the fish ingredient is herring.
61. A process according to claim 60 wherein the herring is in the form of pickled herring.
62. A process according to claim 37 wherein the marine animal ingredient is a crustacean product.

63. A process according to any of preceding claims 37-62 wherein the marine animal ingredient is in the form of pieces having a largest edge length being in the range of 1-50 mm.
- 5 64. A process according to claim 63 wherein the marine animal ingredient pieces have a largest edge length which is in the range of 5-40 mm and preferably in the range of 10-20 mm.
- 10 65. A process according to any of preceding claims 37-64 wherein the content of C20:5 and C22:6 n-3 polyunsaturated fatty acids is at least 1.5 wt%, preferably at least 1.75 wt%, more preferably at least 2.0 wt% and in particular at least 2.25 wt%.
- 15 66. A process according to any of preceding claims 37-65 wherein the marine animal ingredient is an ingredient which has not been subjected to a heat treatment leading to coagulation of the proteins hereof.
- 20 67. A process according to any of preceding claims 37-66 wherein the weight ratio between C20:5/C22:6 n-3 polyunsaturated fatty acids and n-9 polyunsaturated fatty acids in the resulting product is in the range of 1:9 - 1:1, preferably in the range of 1:6.7 - 1:2.7 and more preferably in the range of 1:4 - 1:3.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 92/00344

A. CLASSIFICATION OF SUBJECT MATTER		
IPC5: A23L 1/30, A23L 1/325 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC5: A23L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
WPAT, USPM		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 2217173 (B A WHITTLE), 25 October 1989 (25.10.89), page 7, claims 1-4,6,9,12 --	1,3,5,6,15, 16,23,24
A	US, A, 3793464 (D.T. RUSCH), 19 February 1974 (19.02.74), column 1, line 38; column 2, line 3; column 2, line 50 - line 51, claim 1, abstract --	1,37
A	EP, A2, 0404058 (MILUPA AKTIENGESELLSCHAFT), 27 December 1990 (27.12.90), page 3, line 32, claims 1,7 --	1,37
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search		Date of mailing of the international search report
10 March 1993		15 -03- 1993
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer INGA-KARIN PETERSSON Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 92/00344

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB, A, 2221843 (NORSK HYDRO A S), 21 February 1990 (21.02.90), claims 1,15 --	1,37
A	Patent Abstracts of Japan, Vol 8, No 187, C-240, abstract of JP, A, 59-82070 (KEWPIE K.K.), 11 May 1984 (11.05.84) -- -----	1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 92/00344

The claims refer to a product containing fatty acids, but the examples in the description show oils i.e. esters of the acids.

Claims 1,31,59 and 65 refer to "...a content of C20:5 and C22:6...", but claims 33-37 and 67 to "C20:5/C22:6".

Claim 1 states "10-90 wt% of an oil-in-water emulsion..." but claim 37 "the proportion of the oil-in-water emulsion in the range of 20-80 wt%".

Claim 22 states "...preferably in the range of 4-18 wt%" but claim 56 "...5-18 wt%".

In claim 24 the fish is selected from "...white fish..." but in claim 58 from "...cod...".

INTERNATIONAL SEARCH REPORT

Information on patent family members

29/01/93

International application No.

PCT/DK 92/00344

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2217173	25/10/89	NONE	
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