



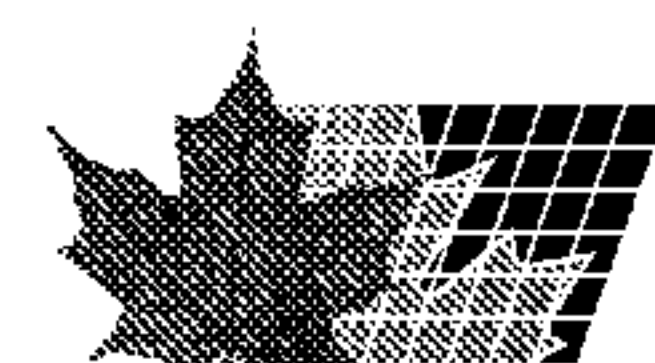
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(72) Inventeurs/Inventors:
WESTER, INGMAR, FI;
ORTE, JUHA, FI
(73) Propriétaire/Owner:
RAISIO BENECOL OY, FI
(74) Agent: OYEN WIGGS GREEN & MUTALA LLP

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(57) **Abrégé/Abstract:**

Olive oil based products, based on the virgin olive oils, containing plant sterol and/or stanol fatty acid ester blends made from high polyunsaturated fatty acid containing vegetable oils are provided. The olive oil based products provide the advantage of incorporating cholesterol-lowering plant stanols and sterols into high grade commercial olive oils, such as virgin olive oils, while avoiding the undesirable precipitation or crystallization of higher melting lipids in higher grade olive oils normally associated with the incorporation of such stanol and/or sterol fatty acid esters by crystallizing any higher melting lipids from the olive oil at temperatures ranging from room temperature to refrigerator temperature. Methods for preparing the olive oil based products are provided.



ABSTRACT OF THE DISCLOSURE

Olive oil based products, based on the virgin olive oils, containing plant sterol and/or stanol fatty acid ester blends made from high polyunsaturated fatty acid containing vegetable oils are provided. The olive oil based products provide the advantage of incorporating cholesterol-lowering plant stanols and sterols into high grade commercial olive oils, such as virgin olive oils, while avoiding the undesirable precipitation or crystallization of higher melting lipids in higher grade olive oils normally associated with the incorporation of such stanol and/or sterol fatty acid esters by crystallizing any higher melting lipids from the olive oil at temperatures ranging from room temperature to refrigerator temperature. Methods for preparing the olive oil based products are provided.

EDIBLE FAT BLENDS

BACKGROUND OF THE INVENTION

5 This invention relates to olive oil based products, based on especially higher grades of olive oils like virgin olive oils, containing plant stanol esters and/or plant sterol esters and methods for preparing such olive oil based products, as well as certain plant stanol and/or sterol esters usable for the preparation of the olive oil based product.

10 Plant sterols are a group of compounds structurally very similar to cholesterol. The plant sterols occurring most frequently in nature are sitosterol, campesterol and stigmasterol. Vegetable oils and fats are the main source of plant sterols in our diet. In vegetable oils a major part of the sterols exists as fatty acid esters. Saturated plant sterols such as sitostanol and campestanol are present in our diet in small amounts. Daily intake of total stanols in the Finnish diet has been estimated to 30-80 mg/day. 15 However, tall oil sterols contain 10-20% of plant stanols (mainly sitostanol and campestanol). Plant stanols can also be produced by hydrogenation to remove the double bond in corresponding plant sterols.

20 In recent years, much interest has been focused on the cholesterol-lowering properties of plant stanols and sterols with already many plant stanol or sterol enriched products such as margarines, salad dressings, bars and yogurts commercially available. Based on recent studies, a daily intake of 2-3 g plant stanols or sterols significantly reduces serum LDL cholesterol levels even when used as part of healthy recommended diets. Plant stanol and sterol enriched foods provide an enhanced dietary approach for lowering elevated serum total and LDL cholesterol 25 levels. Enrichment of staple foods with plant stanols and/or sterols in their fatty acid ester forms is possible without compromising on taste or mouthfeel. Based on the cholesterol lowering efficacy and the fact that plant stanols are virtually unabsorbable, plant stanols are more preferable, but also blends of plant stanols and sterols or plant sterols alone can be used.

30 The best benefit from using plant stanols and/or sterols for lowering elevated serum total and LDL cholesterol levels is obtained when enriching staple foods. For example, in the northern part of Europe, margarine and spreads are very suitable food products for such enrichment, but for the southern part of Europe other staple food candidates need to be found. In this region, olive oil is a staple food of major

importance. In addition, olive oil consumption is increasing also in other parts of the world due to the health reputation and the flavour of higher grades of olive oils. Olive oil contains naturally very low levels of plant sterols (typically < 0.2 g/100 g oil). In addition higher grade olive oils, such as virgin olive oils, contain quite high amounts of squalene, a precursor of cholesterol. The content of squalene varies, but extra virgin olive oil typically contains about 300 mg/100 g oil. Dietary squalene has been shown to increase serum cholesterol levels in man. Such an effect on serum total and LDL cholesterol levels may be counteracted by plant stanols and/or sterols. Therefore, there is clearly a need to make commercially available higher grade olive oils enriched with plant stanols and/or sterols, and to ensure that such olive oils have similar properties as normally used olive oils.

Virgin olive oils should remain clear when stored at 20°C for 24 hours. Typically, higher grades of olive oils, such as virgin olive oils, become cloudy with even clear crystallization occurring when stored for a prolonged time at refrigerator temperatures. An olive oil enriched with plant stanols and/or sterols should avoid cloudiness.

For the large-scale production of plant stanol and/or sterol esters, normally common vegetable oils or commercially available edible oils with modified fatty acid compositions are used. Enrichment of higher grades of olive oils, such as virgin olive oils, with plant stanol and/or sterol esters with fatty acids derived from such commercially available vegetable oils or their blends further enhances the precipitation of higher melting lipids at room temperatures and below. The formed crystals do not normally dissolve, even after prolonged storage at room temperatures. This problem cannot be solved, even by using the esterification of stanol and/or sterol fatty acids derived from currently commercially available vegetable oils with high levels of polyunsaturated fatty acids and low levels of saturated fatty acids, such as low saturated soybean oil (PUFA: 67 weight-%, SAFA: 7,9 weight-%), sunflower oil (PUFA: 64 weight-%, SAFA: 12 weight-%) or linola oil (PUFA: 70 weight-%, SAFA 11 weight-%).

U.S. Patent 5,089,139 describes a method for refining virgin olive oil, in which the virgin olive oil is microfiltrated over a microfilter at temperatures from 15 to 35°C to obtain a virgin olive oil staying bright when subjected to a cold test at 0°C for 24 hours.

U.S. Patent 3,751,569 describes clear cooking and salad oils having hypo-cholesterolemic properties. Into the liquid glyceride base oil is mixed 0.5-10

weight-% (calculated as free sterols) of a sterol fatty acid ester. The fatty acid moiety is defined as a C₁₋₁₂ saturated monocarboxylic acid moiety or an unsaturated fatty acid with up to 24 carbon atoms. In one embodiment, the sterol fatty acid ester is prepared by perchloric acid catalyzed esterification of commercially-available free sterols with monocarboxylic acid anhydrides. The sterol fatty acid ester is added in an amount small enough to prevent precipitation at refrigerator temperatures. In the exemplified embodiment, the cooking or salad oil was prepared by dissolving a liquid glyceride base oil and a plant sterol monocarboxylic acid ester in a mutual solvent (such as hexane or diethyl ether) and evaporating the solvent.

The solubility of different fatty acid esters of plant sterol in triolein are also presented, showing very low solubility for C₁₂ (0.6%) and C₁₆ (0.1%) saturated fatty acid plant sterol esters. The process and product disclosed in the '569 patent suffers from at least two drawbacks. First, the use of fatty acids prepared from individual commercially-available free sterols is neither practical nor economical, as these starting products are quite expensive. Second, the perchloric acid catalyzed esterification process used in the '569 patent is not a food grade process, as residual chloride remains in the product. Thus, the '569 patent is not suitable for commercial applications.

GB Patent 1 405 346 teaches a process by which free sterols naturally contained in edible oils and fats are converted to fatty acid esters via an interesterification process. In addition, in Example 2 a method for producing vegetable oils with elevated sterol ester contents is described. However, the method taught is based on the interesterification of the entire oil blend, which based on physical properties cannot be executed for higher grades of commercial olive oils, such as virgin olive oils.

SUMMARY OF THE INVENTION

Saturation of a plant sterol blend to a corresponding plant stanol blend causes marked differences in the melting properties of the corresponding sterol/stanol esters with the same fatty acid composition. For example, vegetable oil based sterol ester with low erucic acid rapeseed oil fatty acids and corresponding stanol fatty acid ester showed the following amounts of solid fat contents (weight-% of total fat) at different temperatures as measured by NMR-technique:

	10°C	20°C	30°C	35°C	40°C
plant sterol	40.5	11.6	3.5	1.7	1.1
plant stanol	82.3	70.2	34.9	9.4	5.2.

The physical properties of stanol and/or sterol fatty acid esters can be tailor-made by changing the fatty acid composition of the fatty acid ester or by using different ratios of plant stanols and sterols in the ester.

- 5 In the present invention the problem with the precipitation/crystallisation of higher melting lipids in higher grade olive oils is overcome by dissolving plant stanol and/or sterol fatty acid esters with fatty acids derived from so-called high PUFA vegetable oils in higher grade olive oils, such as virgin olive oils, and crystallising any higher melting lipids from the olive oil at temperatures in the range from refrigerator temperatures to room temperatures to obtain a plant stanol and/or sterol
- 10 fatty acid ester blend with a very low content of saturated fatty acid esters contained in the olive oil. The crystallisation temperature and time needed is dependent on the amount and type of stanol and/or sterol fatty acid ester used. By choosing the crystallisation temperature and time properly, the virgin olive oils either stay clear at refrigerator temperatures or become clear when the oil is removed from refrigeration
- 15 and kept at room temperatures for a short period of time. Compared to U.S. Patent 3,751,569, which shows a very limited solubility for e.g. plant sterol palmitate in a liquid glyceride base oil (0.1%), the presence of a plant stanol and/or sterol fatty acid ester blend with a high level of unsaturated fatty acids clearly enhances the solubility of stanol and/or sterol esters.
- 20 In addition, the present invention teaches plant stanol and/or sterol ester compositions usable for direct enrichment of virgin olive oils. Thus, an oil according to the invention can also be obtained by adding the appropriate amount of a plant stanol and/or sterol ester with a fatty acid composition containing more than 60%, preferably more than 65%, polyunsaturated fatty acids, and less than 5%
- 25 saturated fatty acids. When olive oils which are clear at refrigerator temperatures are desired, a plant stanol and/or sterol ester with a fatty acid composition containing more than 60%, preferably more than 65%, polyunsaturated fatty acids, and less than 5% saturated fatty acids, preferably less than 3%, less than 2%, or most preferably less than 1.5% saturated fatty acids, such as stearic acid, is used.
- 30 Such stanol and/or sterol fatty acid esters can be obtained by any esterification method known in the art, such as by esterification of a fatty acid blend or a fatty acid alcohol ester blend having the appropriate predetermined fatty acid composition. All percentage values above and throughout the specification are weight-%, unless otherwise indicated.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "virgin olive oils" is meant to include extra virgin olive oil, virgin olive oil and ordinary virgin olive oil, all defined according to the Official Journal of the European Communities No. L 39/2 (15.2.1992). In addition, any blend of virgin olive oils with lower grades of olive oils as defined by the Official Journal of the European Communities is covered by this definition. Preferably, such a blend contains at least 25%, more preferably at least 50%, and most preferably at least 75% virgin olive oils.

The term "olive oil based product" is meant to include virgin olive oils, according to the above definition, enriched with a blend of plant stanol and/or sterol fatty acid esters. About 0.3-25 weight-%, preferably about 0.3-10 weight-%, more preferably about 1.5-10 weight-%, and most preferably about 3-10 weight-% of plant stanol and/or sterol fatty acid esters (calculated as free stanols) may be included in the olive oil based product.

The term "high PUFA vegetable oils" is meant to include vegetable oils or vegetable oil blends containing more than 50% polyunsaturated fatty acids and at least 7% saturated fatty acids in fatty acid composition. Typical high PUFA vegetable oils include sunflower oil, corn oil, soybean oil, low saturated soybean oil, safflower oil, cottonseed oil, linola oil or their blends. The amount of saturated fatty acids in the fatty acid composition is typically about 7.5-49%, more preferably about 8-25% and most preferably about 10-20%.

The term "phytosterol" is meant to include 4-desmethyl sterols, 4-monomethyl sterols, and 4,4-dimethyl sterols (triterpene alcohols) or their blends. The term "phytostanol" is meant to include 4-desmethyl stanols, 4-monomethyl stanols and 4,4-dimethyl stanols, and is preferably obtained by hydrogenation of the corresponding phytosterol. Typical 4-desmethyl sterols include sitosterol, campesterol, stigmasterol, brassicasterol, 22-dehydrobrassicasterol, Δ^5 -avenasterol. Typical 4,4-dimethyl sterols include cycloartenol, 24-metylenecycloartanol and cyclobranol. Typical phytostanols include sitostanol, campestanol and their 24-epimers, cycloartanol and saturated forms obtained by saturation of triterpene alcohols (cycloartenol, 24-metylenecycloartanol and cyclobranol). The terms phytosterol and phytostanol also include all possible natural blends of 4-desmethyl sterol and stanols, 4-monomethyl sterols and stanols, 4,4-dimethyl sterols and stanols and mixtures of natural blends. The terms phytosterol and phytostanol

further include any individual 4-desmethyl sterol, 4-monomethyl sterol or 4,4-dimethyl sterol or their corresponding saturated (stanol) forms.

The terms "plant sterol" and "plant stanol" are intended to be synonyms to the terms "phytosterol" and "phytostanol", respectively. "Sterol" and "stanol" shall also mean
5 "phytosterol" and "phytostanol", respectively.

"Polyunsaturated fatty acids" are herein defined as fatty acids containing two or more double bonds. Preferably, the double bonds have *cis* configuration, but one or more double bonds may be in *trans* configuration. It is known that many commercially available vegetable oils due to thermal isomerisation in the
10 deodorisation process contain a percentage level of polyunsaturated fatty acids containing one or more double bonds with *trans* configuration. In addition, the double bonds can be either so-called methylene interrupted or conjugated. Typical vegetable oil derived polyunsaturated fatty acids are linoleic, linolenic and γ -linolenic acid, but also polyunsaturated fatty acids from fish oils such as
15 eicosapentaenoic and docosahexaenoic acid can be utilised.

By the term "saturated fatty acids" is meant fatty acids with 4-24 carbon atoms not having any double bonds, thereby including both straight chain and branched fatty acids.

By the term "high PUFA stanol and/or sterol esters" is meant stanol and/or sterol
20 esters produced preferentially with fatty acids from high PUFA vegetable oils, but also fish oil derived polyunsaturated fatty acids or blends of vegetable and fish oil derived polyunsaturated fatty acids can be used.

The stanol and/or sterol fatty acid esters used in the present invention are preferably produced using a food grade process. A "food grade process" is herein defined to
25 include any process whereby the stanol and/or sterol fatty acid ester product is free from residual chemicals which are (1) undesired in the final product because they affect one or more of the qualities of the stanol and/or sterol fatty acid esters, or (2) harmful to a consumer from a food safety standpoint (e.g., the solvents or catalysts contain chlorides). There are a number of food grade processes known in the art,
30 any of which may be suitable for producing the stanol and/or sterol fatty acid esters used in the present invention. Preferably, the food grade process is a solvent free food grade process. The stanol and/or sterol fatty acid esters may be produced by the method described in U.S. Patent 5,502,045, for instance by transesterification of fatty acid alcohol esters obtained from high PUFA vegetable oils or their blends.

Another suitable method for producing the stanol and/or sterol fatty acid esters is by esterification of the free stanol and/or sterol with high PUFA vegetable oils in the presence of a trans- or interesterification catalyst. Esterification of the stanol and/or sterol fatty acid ester may be carried out using an excess of alcohol fatty acid esters, and performing the
5 esterifying step in the presence of an interesterification catalyst. Alternatively direct, preferably catalytic esterification methods such as those disclosed in U.S. Patent 5,892,068, or enzymatic esterification methods such as those disclosed in EP 195 311 may be used.

Another possibility to produce stanol and/or sterol fatty acid esters is to utilise the excess of
10 high PUFA alcohol esters present in the oily phase obtained after the esterification of high PUFA sterol and/or stanol ester according to the method described in U.S. Patent 5,502,045. This mixture of high PUFA alcohol ester and sterol and/or stanol ester can as such be subjected to a fractionation step to remove higher melting sterol and/or stanol esters and then be used for the esterification of the stanol and/or sterol.

15 The stanol esters, sterol esters or their blends can preferably be produced by the method outlined in US patent 5,502,045 using fatty acid alcohol esters with a predetermined fatty acid composition according to the present invention. The fatty acid alcohol esters can be produced by any process known in the art, such as solvent or detergent fractionation of
20 alcohol fatty acid esters obtained from a high PUFA liquid vegetable oil or blends of high PUFA oils. Corresponding blends of fatty acid alcohol esters can also be obtained by distillation procedures under reduced pressure. Such distillation procedures can preferentially be used to remove saturated fatty acids with 16 or less carbon atoms. Fatty acid alcohol esters with the defined fatty acid compositions can also be obtained by
25 alcoholysis of vegetable oils or oil blends with reduced contents of saturated fatty acids, obtained e.g. according to the U.S. Patent 5,670,348.

The stanol and/or sterol esters with the desired fatty acid composition can also be produced by direct, preferably catalytic esterification methods, e.g. U.S. Patent 5,892,068, between
30 free fatty acids or fatty acid blends of the composition and the stanol and/or sterol. Esterification of the stanol and/or sterol with a triglyceride having the desired fatty acid composition using a trans- or interesterification catalyst is also a suitable method to produce the stanol and/or sterol esters. In addition, stanol and/or sterol esters can also be produced by enzymatic esterification e.g. as outlined in EP 195 311.

35 In addition blends of polyunsaturated fatty acids can be used for obtaining stanol and/or sterol esters with the desired composition.

Stanol esters and/or sterol esters with the desired fatty acid compositions can further be obtained by commercially applied fractionation processes, such as dry, detergent and wet-type fractionation of stanol and/or sterol fatty acid esters obtained by esterification of high PUFA fatty acids derived from e.g. vegetable oil or oil blends by methods based on e.g. the transesterification process outlined in U.S. Patent 5,502,045, any direct preferably catalytic esterification process or by the use of an enzymatic esterification process e.g. as outlined in EP 195 311. Especially fractionation from solvents can be used for preparing desired sterol and/or stanol ester compositions. When using enzymatic esterification processes such as outlined in EP 195 311 the fractionation can preferably be carried out directly in the reaction solvent used in the esterification process after removing the enzyme and possible water phase.

The processes discussed above are just a few of the food grade processes which may be used to manufacture the stanol and/or sterol fatty acid esters in accordance with the invention.

In a preferred embodiment virgin olive oils, preferentially an extra virgin olive oil containing a predetermined blend of stanol and/or sterol fatty acid esters can be obtained by dissolving 5-50 weight-% (preferentially 5-25%) of stanol and/or sterol fatty acid esters obtained by an esterification process such as that disclosed in U.S. Patent 5,502,045, for example by using a high PUFA vegetable oil or a mixture of high PUFA vegetable oils as a source for the fatty acids. This can preferentially be carried out as part of the regular refining process of virgin olive oils. The so-obtained stanol and/or sterol ester olive oil blend is heated and mixed to totally dissolve the stanol and/or sterol esters in the olive oil, after which a conventional "winterizing" step or any fractionation process as known in the art is carried out. For example, a winterizing or batch dry fractionation type of process can be carried out at 0-30°C, preferably at 5-25°C resulting in olive oil based products being clear at some point in the temperature range of 4-25°C, more preferably at some point in the temperature range of 4-8°C. All the olive oil based products made in accordance with the invention may become clear, in the cases of showing cloudiness at refrigerator temperatures, when removed from refrigeration and stored at room temperature, i.e. at some point in the temperature range of 18-30°C, more preferably at some point in the temperature range of 18-25°C. This means that the olive oil based product of the invention is clear at 30°C or more, preferably at 25°C or more, more preferably at 20°C or more, even more preferably at 18°C or more. If the product is stored at refrigerator temperatures (i.e., about 2-12°C, preferably about 2-

8°C), it is preferably clear at 8°C, more preferably at 4°C. As European consumers mostly are used to storing the oil at room temperatures, the olive oil based product may preferably be clear at 25°C or more, more preferably at 20°C or more, and most preferably at 18°C or more.

- 5 The crystallisation temperature and time can be altered depending on the amount and type of stanol ester and/or sterol ester used and the desired end product. After removing the solid part mainly made up of saturated fatty acids of the stanol and/or stanol ester by e.g. vacuum filtering, the obtained olive oil based product can be used as such or diluted with unprocessed virgin olive oils to obtain the desired
- 10 content of plant stanol and/or sterol in the olive oil based product. Depending of the quality of the virgin olive oils, some part of the higher melting lipid components naturally contained in the olive oil will simultaneously be removed by the filtering process, and thus the process improves the clarity of the olive oil at refrigerator temperatures (i.e., about 2-12°C, preferably about 2-8°C). It is obvious to those
- 15 skilled in the art that any type of fractionation process in addition to the winterizing or batch dry fractionation type of processes can be utilised for crystallising and removing stanol and/or sterol fatty acid esters with higher melting points, e.g. sterol and/or stanol fatty acid esters based on saturated fatty acids. It is also clear to those skilled in the art that any filtration method known in the art can be used.
- 20 Another way of producing stanol and/or sterol esters with the desired fatty acid compositions is to utilise the excess of fatty acid methyl ester of the high PUFA sterol and/or stanol ester blend obtained after the transesterification disclosed in U.S. Patent 5,502,045. After the drying step, the stanol and/or sterol ester fatty acid alcohol ester mixture is cooled to 5-25°C, depending on the composition of the
- 25 stanol and/or sterol ester produced, and the higher melting components are allowed to crystallize for 4-24 hours. Optionally additional fatty acid alcohol ester is added to facilitate the fractionation process. Any fatty acid alcohol ester may be used, but the use of high PUFA alcohol ester is preferred. After filtration, the clear oily phase is preferably deodorised to remove the excess fatty acid alcohol esters and to obtain
- 30 a tasteless stanol and/or sterol ester. The stanol and/or sterol esters obtained as such can preferably be mixed into the virgin olive oils.

Plant stanol and/or sterol fatty acid esters with the desired fatty acid composition can furthermore be produced from fatty acids or fatty acid alcohol esters with appropriate composition. The so-obtained plant stanol and/or sterol fatty acid esters

35 can be added directly to virgin olive oils to obtain olive oil based products taught by this invention.

In addition stanol and/or sterol ester compositions according to the invention can be produced utilising "fatty acid starting materials" such as fatty acids, fatty acids alcohol esters or oils obtained by processes including e.g. utilising of micro-organisms, enzymes or new breedings of oil producing plants. The sterol and/or stanol part may be obtained from any sterol and/or stanol source, e.g. from the paper pulping industry or from the processing of vegetable oils. New breedings producing elevated amounts or more attractive compositions of suitable sterols and/or stanols produced by conventional methods or genetic modifications are also included as possible raw-materials for the production of stanols and/or sterols. Preferably, the stanol and/or sterols are thereafter utilized in a food grade process to produce the olive oil based product of the invention.

In a preferred embodiment of this invention, virgin olive oils are enriched with plant stanol fatty acid esters with a predetermined fatty acid composition. Also blends of plant stanol and sterol fatty acid esters or plant sterol fatty acid esters can be used.

The following examples are presented in order to disclose the present invention in more detail. All the percentages given are in weight-%.

EXAMPLES

Example 1: Preparation of stanol fatty acid esters based on low saturated soybean oil fatty acids (LowSatSoy)

The plant stanol fatty acid esters were produced in a pilot scale. 6 kg plant stanols (composition: 68.2% sitostanol, 28.3% campestanol, 1.1% sitosterol and trace amounts of other unsaturated sterols) obtained by hydrogenation of commercially available plant sterols was blended with 8.6 kg LowSatSoy methyl ester mixture and dried at 110-120°C. The temperature of the dry mixture was reduced to 90-95°C and the sodium methylate catalyst (73 g) was added. The temperature was increased to 120°C and the reaction was carried out under vacuum (40 mmHg) for 4 hours. The conversion was monitored by GC analysis. Once >98% conversion was achieved, the temperature was reduced to 100°C and 30 weight-% hot, >90°C water was added to destroy the catalyst. The water phase was removed and the oily phase was rewashed to provide a soap content <1000 ppm. The oily phase was dried at 95°C and the dry material was bleached using 1 weight-% bleaching aid (Trisyl, Grace, Germany) for 20 minutes at 95°C under vacuum. After removal of the bleaching aid by filtration, a standard pilot scale deodorization (batch deodorizer, capacity 9 kg) was carried out to remove the excess of soybean oil methyl esters and to obtain a

tasteless stanol ester product. The fatty acid composition of the obtained plant stanol ester was as follows: SAFA: 8.7%, MUFA: 27.5% and PUFA: 63.8%. The content of C16:0 and C18:0 was 3.6% for both. The stanol content was 57.6 weight-% with a high esterification conversion (amount of free stanol 1.5 weight-%).

5 Example 2: Preparation of vegetable oil based stanol fatty acid ester with fatty acids derived from linola oil

A stanol fatty acid ester blend with fatty acids derived from linola oil was prepared with same plant stanol blend and method as outlined in Example 1. The fatty acid composition of the obtained plant stanol ester was as follows: SAFA: 10.6%,
10 MUFA: 17.7% and PUFA: 71.8%. The content of C16:0 and C18:0 was 6.2% and 3.9% respectively. The stanol content was 57.9 weight-% with a high esterification conversion (amount of free stanol 0.13 weight-%).

Example 3: Preparation of plant stanol fatty acid ester based on distilled high PUFA fatty acids derived from sunflower oil

15 High PUFA plant stanol esters was produced with similar procedures as outlined in Example 1 with methyl fatty acid esters obtained after distillation of sunflower oil based methyl esters. The combined distillation cuts contained 5.6% SAFA (0.3% C16:0, 5.0% C18:0), 26.5% MUFA and 67.9% PUFA. The total sterol (plant sterol + plant stanol) content of the plant stanol ester was 59.5%, whereas the plant stanol
20 content was 58.4 weight-%. The amount of free stanols was 0.86 weight-%.

Example 4: Preparation of plant stanol ester enriched virgin olive oil by crystallisation at + 7°C.

7 weight-% of the plant stanol ester (equivalent to 4.0 weight-% of plant stanols and 0.05 weight-% of plant sterols) with fatty acids derived from LowSatSoybean oil
25 produced according to Example 1 was dissolved in extra virgin olive oil (Carlshamn Mejeri, Sweden) by heating the oil to 60°C and stirring at normal pressure. When all plant stanol ester had dissolved the blend was left to crystallise under slow stirring at + 7°C for 21 hours. The oil was filtered by using vacuum (40 mmHg) and thick (carbon) filtration paper used conventionally in winterization processes. The weight
30 of the filtrate was 1.1 weight-% of the initial extra virgin olive oil plant stanol ester blend. The obtained olive oil based product contained 3.7 weight-% plant stanol with 0.12 weight-% plant stanols being in the free form. The fatty acids of the plant stanol ester contained 4.9% saturated fatty acid (2.4% C16:0 and 1.5% C18:0), compared with 8.7% saturated fatty acids in the added plant stanol ester, clearly

showing that it was mainly saturated plant stanol esters that crystallised. The plant stanol content of the filtrate was 19.3 weight-% with only 0.18 weight-% plant stanol in the free form. The obtained plant stanol ester enriched virgin olive oil stayed clear at 5°C for at least 5 days, while clear crystallisation of the glass wall of the bottle could be seen after 3 days in the control extra virgin olive.

Example 5: Preparation of plant stanol ester enriched virgin olive oil by crystallisation at 16°C

A plant stanol ester enriched extra virgin olive oil was similarly prepared as in Example 4, except that the crystallisation was carried out at 16°C for 21 hours. The obtained olive oil based product contained 3.7 weight-% plant stanol with 0.11 weight-% plant stanols being in the free form. The fatty acid composition of the plant stanol ester was 4.5% SAFA (2.3% C16:0 and 1.4% C18:0), 29.0% MUFA and 66.6% PUFA. The weight of the filtrate was 1.5 weight-% of the initial virgin olive oil stanol ester blend. The plant stanol content of the filtrate was 10.7 weight-%, with only 0.1 weight-% as free plant stanol. The fatty acid composition of the plant stanol ester of the filtrate was 36.9% SAFA (18.9% C16:0 and 15.4% C18:0), 19.7% MUFA and 43.4% PUFA. This data clearly shows that mainly saturated fatty acid plant stanol esters are crystallised. The obtained plant stanol ester enriched virgin olive oil stayed clear at 5°C for at least 5 days, while clear crystallisation of the glass wall of the bottle could be seen after 3 days in the control extra virgin olive oil.

Example 6: Preparation of plant stanol ester enriched virgin olive oils

7 weight-% of plant stanol ester produced according to Example 2 was dissolved in extra virgin olive oil (Carlshamn Mejeri, Sweden) according to Example 4 and crystallised at 16°C for 20 hours. The oil sample obtained after filtration was stored in a refrigerator at 7°C for 24 hours and was found to become cloudy. The sample became clear at room temperature, but started to become cloudy after one day at room temperature, with clear crystal formation after 2 days at room temperature. The obtained olive oil based product contained 3.3 weight-% of plant stanol. The fatty acid composition of the plant stanol ester was 6.0% SAFA, 19.4% MUFA and 74.6% PUFA, compared to source linola stanol ester 10.6% SAFA, 17.7% MUFA and 71.8% PUFA. Based on this data it is clear that a SAFA content of 6% of the fatty acids of the plant stanol ester is too high to obtain the desired properties of the olive oil based product.

Example 7: Preparation of plant stanol ester enriched virgin olive oils

11 and 16 weight-% of the plant stanol ester obtained in Example 3 was dissolved in extra virgin olive oil (Carlshamn Mejeri, Sweden) and processed according to Example 4. The crystallisation temperatures were +7°C (20 hours) and +23°C (7 days) for the 16 weight-% samples and +23°C (7 days) for the 11 weight-% sample. The 16 weight-% sample crystallised at 7°C remained clear at 7°C for at least 1 week. The total stanol content of this olive oil based product was 8.9 weight-% and the fatty acid composition of the plant stanol ester contained in the olive oil based product was 1.7% SAFA (0.65% C16:0 and 0.34% C18:0), 26.8% MUFA and 71.5% PUFA. This olive oil based product can be diluted with unprocessed virgin olive oils to obtain desired plant stanol content of the olive oil based product to commercialise.

The samples crystallized at 23°C for 7 days became cloudy at 7°C, but both samples became clear at room temperature. The stanol content of the two olive oil based products was 6.3 and 8.9 weight-% for the 11% and 16% samples, respectively.

Example 8: Preparation of plant stanol ester enriched virgin olive oils

4.5 weight-% of the plant stanol esters obtained in Examples 1, 2 and 3 was dissolved in extra virgin olive oil (Carlshamn Mejeri, Sweden) and stored at 7°C for 11h. The olive oil based products enriched with plant stanol ester based on sunflower methyl ester cuts (SAFA: 5.6%; C16:0 0.3%, C18:0 5.0%) showed clear crystallisation at +7°C and these samples did not become clear at room temperature clearly indicating that the amount of C18:0 stanol ester is too high in this olive oil based product. All three blends also crystallised because the SAFA content was too high (8.7%, 10.6% and 5.6%).

Example 9: Preparation of plant stanol fatty acid ester with desired fatty acid composition by solvent fractionation

10 g of the plant stanol ester obtained by the procedure outlined in Example 1 was dissolved in 90 ml n-hexane in a 200 ml centrifuge tube. The mixture was kept at +7°C for 24 hours, after which the mixture was centrifuged in a temperature programmable centrifuge. The hexane phase was removed and the hexane was evaporated. The obtained plant stanol ester contained 4.6% SAFA (2.4% C16:0 and 1.8% C18:0), 27.2% MUFA and 68.2% PUFA.

Example 10: Preparation of an olive oil based product using plant stanol ester with desired fatty acid composition

7 weight-% of the plant stanol ester obtained from example 9 was dissolved in extra virgin olive oil according a similar procedure as outlined in Example 4 and stored at
5 +7°C. The oil remained clear for at least 7 days.

Example 11: Preparation of an olive oil based products enriched with stanol fatty acid esters

Two batches of fatty acid methyl esters were prepared by distillation in a similar way as described in Example 3, but with the following obtained fatty acid
10 compositions: 4.9% SAFA, 34.1% MUFA and 61% PUFA and the other 2,5% SAFA, 36,5% MUFA and 61% PUFA. The obtained fatty acid methyl esters were used for esterification of plant stanol using the method described in Example 1. 0.3 g of the stanol fatty acid esters was dissolved in 10 g extra virgin olive oils Both oils remained clear at room temperature for at least a week.

15 Example 12: Preparation of an olive oil based product enriched with sterol fatty acid ester

The same fatty acid methyl ester comprising 4.9% SAFA, 44.1% MUFA and 61% PUFA as prepared and used in Example 11 was used for esterification of
20 plant sterol. 0.6 g of the sterol fatty acid ester was dissolved in 10 g extra virgin olive oil. The oil remained clear at room temperature for at least a week.

WHAT IS CLAIMED IS:

1. An olive oil based product, comprising (1) at least one virgin olive oil and (2) a blend of sterol and/or stanol fatty acid esters, wherein the fatty acid portion of the blend contains less than 5 weight-% saturated fatty acids and more than 60 weight-% polyunsaturated fatty acids.
2. The olive oil based product according to claim 1, wherein the fatty acid portion of the blend contains more than 65 weight-% polyunsaturated fatty acids.
3. The olive oil based product according to claim 1 or 2, wherein the fatty acid portion of the blend contains less than 3 weight-% saturated fatty acids.
4. The olive oil based product according to any one of claims 1-3, wherein the fatty acid portion of the blend contains less than 2 weight-% stearic acid.
5. The olive oil based product according to any one of claims 1-3, wherein the fatty acid portion of the blend contains less than 1.5 weight-% stearic acid.
6. The olive oil based product according to any one of claims 1-5, wherein the product is clear at 30°C.
7. The olive oil based product according to any one of claims 1-5, wherein the product is clear at 25°C.
8. The olive oil based product according to any one of claims 1-5, wherein the product is clear at 20°C.
9. The olive oil based product according to any one of claims 1-5, wherein the product is clear at 18°C.
10. The olive oil based product according to any one of claims 1-5, wherein the product is clear at 8°C.
11. The olive oil based product according to any one of claims 1-5, wherein the product is clear at 4°C.
12. The olive oil based product according to any one of claims 1-5, wherein the product becomes clear when its temperature is raised from refrigerator temperature to room temperature.

13. The olive oil based product according to any one of claims 1-12, wherein the at least one virgin olive oil comprises extra virgin olive oil.
14. The olive oil based product according to any one of claims 1-13, wherein the sterol and/or stanol fatty acid ester comprises stanol fatty acid esters.
- 5 15. The olive oil based product according to any one of claims 1-14, wherein the stanol part of the stanol fatty acid ester comprises sitostanol.
16. The olive oil based product according to any one of claims 1-15, wherein the blend (2) is present in an amount of 0.3-10 weight-%, calculated as free sterols and/or stanols.
- 10 17. The olive oil based product according to any one of claims 1-16, wherein the blend is prepared using a food grade process.
18. A method for preparing an olive oil based product, comprising (1) at least one virgin olive oil and (2) a blend of sterol and/or stanol fatty acid esters wherein the fatty acid portion of the blend contains less than 5 weight-% saturated fatty acids and
- 15 more than 60 weight-% polyunsaturated fatty acids, the method comprising
- (a) esterifying a sterol and/or stanol with a source of fatty acids containing less than 5 weight-% saturated fatty acids and more than 60 weight-% polyunsaturated fatty acids, to produce the blend of sterol and/or stanol fatty acid esters and
- (b) dissolving the blend in the at least one virgin olive oil, to obtain the olive
- 20 oil based product.
19. The method according to claim 18, wherein the source of fatty acids contains more than 65 weight-% polyunsaturated fatty acids.
20. The method according to claim 18 or 19, wherein the source of fatty acids contains less than 2 weight-% stearic acid.
- 25 21. The method according to any one of claims 18-20, wherein the esterifying step comprises interesterifying the sterol and/or stanol using an excess of alcohol fatty acid esters, and performing the esterifying step in the presence of an interesterification catalyst.

22. The method according to any one of claims 18-21, wherein the sterol and/or stanol fatty acid esters comprise stanol fatty acid esters.
23. The method according to any one of claims 18-22, wherein the esterifying step is conducted using a food grade process.
- 5 24. A method for preparing an olive oil based product, comprising (1) at least one virgin olive oil and (2) a blend of sterol and/or stanol fatty acid esters, wherein the fatty acid portion of the blend contains less than 5 weight-% saturated fatty acids and more than 60 weight-% polyunsaturated fatty acids, the method comprising
- (a) dissolving plant stanol and/or sterol fatty acid esters having fatty acids
10 derived from high polyunsaturated fatty acids (PUFA) vegetable oils in the at least one virgin olive oil and
- (b) crystallising higher melting lipids from the oil obtained from step (a) at a temperature between 0-30°C, to obtain the olive oil based product.
25. The method according to claim 24, wherein more than 65 weight-% of the
15 fatty acid portion comprise polyunsaturated fatty acids.
26. The method according to claim 24 or 25, wherein less than 2 weight-% of the fatty acid portion comprise stearic acid.
27. The method according to any one of claims 24-26, wherein the crystallising step is preformed at a temperature between 5-25°C.
- 20 28. The method according to any one of claims 24-27, wherein the sterol and/or stanol fatty acid esters comprise stanol fatty acid esters.
29. The method according to any one of claims 24-28, wherein the blend is prepared using a food grade process.
30. A plant sterol and/or stanol fatty acid ester blend, wherein the fatty acid
25 portion of the blend comprises more than 60 weight-% polyunsaturated fatty acids and less than 5 weight-% saturated fatty acids, wherein less than 2 weight-% of the blend comprises stearic acid.

31. The sterol and/or stanol fatty acid ester blend according to claim 30, wherein the fatty acid portion of the blend comprises more than 65 weight-% polyunsaturated fatty acids.
32. The sterol and/or stanol fatty acid ester blend according to claim 30 or 31,
5 wherein less than 1.5 weight-% of the blend comprises stearic acid.
33. The sterol and/or stanol fatty acid ester blend according to any one of claims 30-32, wherein the fatty acid portion of the blend comprises less than 3 weight-% saturated fatty acids.
34. The sterol and/or stanol fatty acid ester blend according to any one of claims
10 30-33, wherein the fatty acids each contain 4-24 carbon atoms.
35. The sterol and/or stanol fatty acid ester blend according to any one of claims 30-34, wherein the blend contains stanol fatty acid ester and the sterol portion comprises sitostanol.
36. The plant sterol and/or stanol fatty acid ester blend according to any one of
15 claims 30-35, wherein the blend is prepared using a food grade process.