

Nutritive Compositions Containing Fatty Substances and
a Process for the Preparation Thereof.

This invention relates to nutritive
5 compositions containing fatty substances, and to a
process for the preparation of said compositions from
fruits of the Ribes genus.

Most vegetable oils contain linoleic (6,9-
10 octadecadienic) and α -linolenic (9,12,15-octadecat-
rienic) polyunsaturated fatty acids. Only oils of the
seeds of hops (Humulus), of hemp (Cannabis), of borage
(Borage) and of evening primrose (Oenothera) are known
as containing γ -linolenic (6,9,12-octadecatrienic)
acid, evening primrose being the only available source
15 at, moreover, a high price.

γ -Linolenic acid is an essential fatty acid
which is metabolised by the organism into prostaglandins
via dihomogamma-linolenic acid and arachidonic acid
(5,8,11,14-eicosatetraenic), which is itself a
20 constituent of cellular membranes, whereas α -linolenic
acid does not take part in the same way in this metab-
olic process. The linoleic acid conversion into
 γ -linolenic acid in the tissue is incomplete (4-20%
compared to 90-98% for the conversion of γ -linolenic
25 acid into arachidonic acid) and may not even exist
(for example in cats) in the case of the absence or the

the inactivation of the enzyme Δ -6-desaturase.

In effect, a lack of essential fatty acids results in a nutritional deficiency affecting all the metabolic processes which have been mentioned above and which may result in biochemical disorders or in organic lesions (for example coagulation disorders, dermatological lesions, endocrinal complaints, myocardiac lesions, and hepatic, articular, neurological and mental disorders). Therefore, it is possible to see the advantages provided by a supply of γ -linolenic acid for the prevention or for the treatment of these anomalies.

The possibility of using γ -linolenic acid and arachidonic acid as therapeutic and nutritional agents has been mentioned in, for example French Patents Nos. 2,197,605 and 1,603,383, γ -linolenic acid being of a synthetic origin or being extracted from the oil of evening primrose (Oenothera) or officinal borage (Borago officinalis) seeds.

Moreover, French Patent No. 2,255,055 relates to cosmetic or pharmaceutical compositions based on the oil of raspberry pips, the anti-inflammatory activity of which is mentioned, but with no indication of the composition. Since the oil is preferably extracted using chloroform (a polar solvent), the anti-inflammatory activity is probably due to the

(12)

presence of minor components. Moreover, analysis of this oil has shown that it contained about 54% by weight of linoleic acid and 30% of a α -linolenic acid, but did not contain any γ -linolenic acid.

5 Finally, Hungarian Patent No. T 1322A states that the addition of a pulp or a crude oil extracted from paprika, tomato or redcurrant pips to cosmetic products or table oils would inhibit their oxidation. The extraction, as it is described, does not
10 allow the separation of the undesirable waxes and colourings in the products which are envisaged, and the composition of the extract is not mentioned.

 Surprisingly, it has been found that oils of pips of fruit of the Ribes genus contain an appreciable
15 percentage, at least 4% by weight, of γ -linolenic acid. Moreover, these pips are available in large quantities in the cakes resulting from squeezing fruit juices, from the production of preserves and jellies or from fermentation musts resulting from the production of
20 brandies, liqueurs and schnapps, by-products which have been used up until now as fuel or forage.

 The present invention relates to nutritive compositions (as herein defined) which contain from 0.61 to 80% by weight of a fatty substance extracted from pips of fruit of the Ribes genus which fatty sub-
25 consists of triglycerides in which γ -linolenic acid represents at least 4% by weight of the fatty acids and which is substantially free from

odorous compounds, the free fatty acids, the colourings and the waxes naturally present in the oil of the pips of fruits of the Ribes genus.

As used in the context of this invention, the term "nutritive composition" designates cosmetic, dermatological (corrective cosmetic) or topical (for example ophthalmic) compositions and dietetic foods or food supplement, or pharmaceutical compositions for oral, enteral or parenteral nutrition.

According to the present invention, the fatty substances entering into the nutritive composition originate in practice from blackcurrants (Ribes nigrum), redcurrants (Ribes rubrum), gooseberries (Ribes ova-
crispa or grossularia) or from hybrid fruits of these species. Of course, a mixture of these fruits may be used.

The lipid content of the by-products mentioned above is from 12 to 30% by weight, depending on the starting material. For its part, the lipid phase contains from 4 to 19% by weight of γ -linolenic acid.

As an indication, the oil of the pips of these fruits comprises triglycerides of the following fatty acids, by weight:

Fatty Acids	Blackcurrants	Red Currants	Gooseberries
C 16 : 0	6 - 7 %	4 - 5 %	7 - 8 %
C 18 : 0	1 - 2 %	1 - 2 %	1 - 1 %
5 C 18 : 1 cis	9 - 10 %	14 - 15 %	15 - 16 %
C 18 : 1 trans	0.5 %	0.5 - 1 %	1 - 2 %
C 18 : 2 ω 6	47 - 49 %	41 - 42 %	39 - 41 %
C 18 : 3 ω 6	15 - 19 %	4 - 5 %	10 - 12 %
C 18 : 3 ω 3	12 - 14 %	29 - 31 %	19 - 20 %
10 C 18 : 4 ω 3	3 - 4 %	2.5 - 3.5 %	4 - 5 %

Blackcurrant oil which is preferred due to its high content of γ -linolenic acid also contains from 1 to 2% by weight of unsaponifiable substances, such as aliphatic alcohols, hydrocarbons, tocopherols, squalene, β -sitosterol, campesterol and Δ -7 stigmasterol. Its density is 0.9215 g/cm³ (at 20°C), and its viscosity is 28.3 mPaS (centipoise) (at 20°C).

A cosmetic or dermatological composition may be presented in the form of a fluid water-in-oil or oil-in-water emulsion (milk, lotion, shampoo, shaving foam, etc.,) or in the form of a thicker emulsion (cream, face pack), and it generally contains from 1 to 20% by weight of the fatty substance mentioned above. Alternatively it may be anhydrous and essentially comprise an oil phase (balm, bath oil, etc.) or it may have a predominant water phase (capillary rinsing product, etc.). In general the oil phase, whether the composition is aqueous or

anhydrous, contains 1 to 80% by weight, based on the total weight of the oil phase, of the fatty substance mentioned above. Finally, the cosmetic or dermatological composition may be essentially solid (make-up products, eye shadow, foundation, lipstick, etc.) and may contain from 1 to 30% of the fatty substance mentioned above.

In addition to containing the fatty substance mentioned above, the fat phase of the composition may contain vegetable, animal, mineral or synthetic oils, waxes, long chain alcohols and polymers which are presently used in cosmetics.

If emulsions are concerned, the compositions contain from 1 to 20% by weight of emulsifiers.

Moreover, the compositions may contain colouring agents, perfumes, preservatives, pigments, lustrants, antioxidants and extenders.

Among the dietetic foods or food supplements which are envisaged, it is possible to mention infants' milk and more particularly milk having the composition of mother's milk, sauces, mayonnaise and oils for salads. In these products, the fatty substances are compounded so that they provide the equivalent of from 0.35 to 2.5% by weight of γ -linolenic acid and represent from 0.61 to 15% by weight. The fatty substances will advantageously be protected from oxidation by the addition of fatty acid esters of ascorbic acid, for example ascorbyl palmitate.

It is also possible to envisage using the

fatty substances mentioned above in animal nutrition, in particular in feeds, for example meat compositions for cats.

5 Finally, the fatty substances mentioned above may enter into the composition of medicaments which have a formulation adapted to the method of administration and are administered, for example, in the form of a syrup or capsules or ocular isotonic emulsions, or they may be constituents of the oil phase of emulsions
10 or combined with oils intended for parenteral nutrition, and they may represent from 5 to 80% by weight of the composition.

In every case, the pharmaceutical compositions according to the present invention will be

15 stabilised physically and chemically (in particular against oxidation) and those for parenteral use presented in sterile, pyrogen-free form.

The present invention also relates to a process for the preparation of fatty substances from
20 pips of fruit of the Ribes genus, characterised in that a vegetable material containing these pips is ground and is extracted by solvents in order to obtain a fatty substance which consists of triglycerides in which γ -linolenic acid represents at least 4% by weight of the fatty acids and which is substantially free from the odorous
25 compounds, the free fatty acids, the colourings and the waxes naturally present in the oil of the pips of fruits of the Ribes genus.

According to the present invention, the term "vegetable material" which is used is understood as designating pips of fruits of the Ribes genus, particularly the by-products which have been mentioned above. The starting material is generally in the form of strongly coloured cakes containing the waxes associated with the pips, waxes and colourings representing from 5 to 7% by weight of the crude oil which would be extracted therefrom, for example using hexane. The waxes are saturated and mono-unsaturated esters of long chain fatty acids with fatty alcohols which are solid at ambient temperature. The waxes and colourings in question are not desired in an oil incorporated in nutritive compositions.

A preferred starting material is the cake obtained by squeezing fruit juices, in particular blackcurrant juice. The cake is initially dried, for example in air for about 1 hour at about 60°C. It is coarsely ground and sieved in order to obtain particles of from 1 to 1.5 mm, the sieving yield ranging from 60 to 80% by weight of the cakes. It is possible to separate advantageously the seeds from the cnaff by gravity in a flow of air or by elutriation with a yield by weight of from 80 to 90%.

According to a preferred embodiment of the present process, the seeds are washed with a conventional polar solvent in order to free them from waxes,

colourings and free fatty acids. For cosmetic uses, it is possible to use, for example methanol, isopropanol, acetone, ethanol or a mixture of these solvents, or a supercritical fluid, for example carbon dioxide under conditions which impart thereto a polar character. For nutritional and pharmaceutical uses, a food-grade solvent will be used, for example ethanol or supercritical carbon dioxide.

By way of example, washing is carried out by extracting the seeds with ethanol under reflux, either in batches, for example at first for about 2 hours and then for about 30 to 60 minutes, or continuously for about 2 hours, then the residue is drained.

In a variant, it is possible to extract the seeds using, for example, carbon dioxide under from 250 to 350 bars and at 60 to 80°C in a continuous cycle, the solvent being recovered in gas form by lowering the pressure, then being recompressed and recycled. It has been found that extraction makes it possible to remove most of the colouring materials and the waxes present in the skins and around the pips. In effect, the waxes are precipitated on cooling from the alcoholic extract, whereas said extract is very strongly coloured.

The drained residue is ground (e.g. particles from 100 to 300 μm), from about 10 to 15% by weight of

water are added, and it is then made into pellets or granules by extruding the paste and cutting the strand. In a variant, it is possible to flake the seeds on a flattening cylinder from the non-ground drained residue. These forms prevent clogging and facilitate the subsequent extraction of the oil by providing the product with a porosity permitting a good penetration of the solvent, and the flakes in particular resist crushing.

The next stage comprises extracting the oil with a non-polar solvent, for example hexane, in a proportion of about 250% by weight of hexane with respect to the residue. In a variant, it is equally possible to use in this stage liquid carbon dioxide or preferably supercritical carbon dioxide under conditions in which it is slightly polar, for example under from 200 to 300 bars and at 40 to 60°C. Of course, it is possible to use, for example, supercritical carbon dioxide in the washing stage and in the subsequent extraction stage, or in only one of these stages, the other being carried out using, for example ethanol or hexane.

After extraction, it is possible, although these measures are only preferred options, to neutralize the solution with concentrated alkali to remove the residual free fatty acids, after having partially evaporated the solvent, for example with a solution containing from 80 to 90% by weight of

solvent is obtained, for example in the case of hexane, so that it contains about 10% by weight of oil. In particular concentrated (e.g. 2N) potassium or sodium hydroxide can be used for neutralization. The solution may be cooled to about 0 to 4°C for about 24 hours, and filtered, preferably at this temperature, in order to completely remove the residual waxes and the solvent is removed by evaporation.

Likewise, the subsequent decolorization and deodorization operations are preferred options: the solution is decolorized using 2 to 8% by weight of active carbon with respect to the oil treated, at from 20 to 60°C, then the hexane is evaporated. The oil is then deodorized by steam stripping at from 140 to 220°C and preferably at about 180°C under a vacuum equal to or less than 1 torr.

According to one variant for the preparation of the oil, the seeds which have been ground are not previously washed, but are directly extracted with a solvent. In this case, the neutralization, the removal of the waxes by decantation, the decolorization and the deodorization as indicated above are essential for the production of a pale yellow refined oil.

In some cases, a fatty substance is to be enriched with γ -linolenic acid. In order to do this, the oil which is freed from waxes and free fatty acids naturally present in the oil of the pips of fruits of the Ribes genus is saponified with an alkali metal hydroxide for example, in a water-alcohol medium, for example, potassium hydroxide in a medium of

methanol/water in a concentration of about 11%, the resulting salts are acidified using a concentrated mineral acid, for example 2N sulphuric acid, the free fatty acids are extracted with a non-polar solvent such as hexane, and the organic phase is separated and dried, for example by the addition of sodium sulphate. In a variant, it is possible to directly treat the ground cake with an alkali hydroxide, to acidify it using a mineral acid, to extract the free fatty acids with hexane and to dry the organic phase as indicated above. The organic phase is fractionated by high performance chromatography in liquid phase, by passage over columns of silica gel loaded with silver nitrate and elution preferably with a mixture of dichloromethane, toluene and diethyl ether at ratios in the range 70:25:5 to 65:30:5 in isocratic manner, i.e., with recycling of the solvent mixture of fixed composition, and a fraction containing about 60% by weight of γ -linolenic acid and about 40% of α -linolenic acid is thus obtained.

Practically pure γ -linolenic acid may be isolated by high performance liquid phase chromatography with a C_8 or C_{18} support in inversed phase with a solvent gradient, for example of a solvent mixture acetonitrile/water, methanol/water or isopropanol/water.

The following examples illustrate the present invention. In these Examples, the parts and percentages are based on the weight.

EXAMPLE 1

100 kg of residue obtained by the extraction of blackcurrant juice and drying are treated a first time for 2 hours under reflux with 250 kg of ethanol and a second time for 1 hour under reflux with 250 kg of ethanol. The residue is drained and is dried twice at 80°C over a period of 30 minutes in an air drier, and is finally ground in a hammer mill.

After moistening with from 10 to 15% of water and after extruding the paste in the form of pellets, the 82 kg of product which is obtained are extracted twice with 205 kg of hexane under reflux for 3 hours, then cooled and filtered. The hexane is then evaporated and 14.3 kg of a clear yellow oil are obtained, the weight content of free fatty acids of which is 0.16%.

EXAMPLE 2

100 kg of dried residue resulting from the extraction of blackcurrant juice are ground in a hammer mill, and the powder is sieved in order to obtain particles of from 1 to 1.5 mm with a sieving yield of from 60 to 80%. The product is moistened and made into pellets and then extracted with hexane, as in Example 1. Part of the hexane is evaporated, the free fatty acids are neutralized with a 2N solution of sodium hydroxide, the organic phase is separated, is left to settle at 4°C for 24 hours and is separated by filtration from

the hard waxes which have settled. The organic phase is treated with from 2 to 8% of active carbon based on the quantity of oil in solution, then the solvent is evaporated and the oil is deodorized by stripping with steam at 180°C under a vacuum of 0.1 torr. From 13 to 16 kg of refined oil are thus obtained.

EXAMPLE 3

100 kg of dried blackcurrant pulp resulting from juice squeezing are ground in a disc mill and the ground product is sieved in order to obtain 60.5 kg of particles of from 1 to 1.5 mm. The product is introduced into an elutriator and 49.5 kg of a heavy fraction essentially comprising seeds are recovered. The fraction is washed twice with each time 120 kg of ethanol under reflux. The process is continued as stated in Example 1, except that the dried residue is made into flakes using a flattening cylinder mill instead of the extruder, and the flakes are extracted with two times 102.5 kg of hexane. 11.1 kg of a clear, yellow oil are obtained.

Examples 4 to 14 : Cosmetic compositions

4 - Care cream (water-in-oil emulsion) % by weight

	Isopropyl myristate	30
5	Liquid paraffin	18
	Blackcurrant oil	10
	Ozokerite	4
	Magnesium lanolate	14.4
	Lanolin alcohol	3.6
10	Butyl hydroxy anisole (BHA) + butyl hydroxy toluene (BHT)	0.01
	Water + preservative: quantity sufficient for	100 %

15 5 - Body milk % by weight

	Liquid paraffin	8
	Blackcurrant oil	3
	Glycerol stearate	2
	Tween 60 (polyoxyethylene (20) sorbitan monostearate) *	1
20	Stearic acid	1.4
	Triethanolamine	0.7
	Carbopol 940* (neutralized)	0.2
	BHA + BHT	0.01
25	Perfume	1
	Water + preservative quantity sufficient for	100 %

* Tween and Carbopol are Registered Trade Marks

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6 - Balm % by weight

	Ozocerite	4
	Blackcurrant oil	12
	Miglyol gel *	30
5	Vaseline *	20
	Soya oil	15
	Sunflower seed oil	19

* Miglyol and Vaseline are Registered Trade Marks

7 - Body Oil % by weight

10	Blackcurrant oil	30
	Soya oil	10
	Sunflower seed oil	30
	Peanut oil	29.8
	BHA + BHT	0.2

15

8 - Face pack % by weight

	Blackcurrant oil	10
	Cetyl alcohol	3
	Stearyl alcohol	3
20	Polyoxyethylene (20) sorbitan mono-oleate (Polysorbate 80)	4
	1,2-propylene glycol	5
	Glycerol	2
	Titanium dioxide	3.5
25	Preservative	0.3
	Distilled water, perfume concentrate	

antioxidant (BHA + BHT) quantity

sufficient for

100 %

Plant extracts or biological extracts may be added as
desired

5

9 - Shaving cream

% by weight

Blackcurrant oil

9.4

Stearic acid

7

Cetyl alcohol

0.7

10 Polyethylene glycol monostearate

3.5

BHA + BHT

0.05

Glycerol

9

Preservative

0.3

Triethanolamine

2.7

15 Perfume and water quantity

sufficient for

100 %

10 - Eye shadow

% by weight

Talc

50

20 Wheat starch

12

Zinc stearate

3

Ultramarine blue

4.5

Yellow iron oxide

3:2

Black iron oxide

0.5

25 Brown iron oxide

0.8

Chromium oxide

2.5

27

	Titanium mica	10
	Titanium mica + iron oxide	3.5
	Agglomerating agent	10
	Formula of the agglomerating agent:	<u>% by weight</u>
5	Liquid paraffin	50
	Liquid lanolin	20
	Blackcurrant oil	20
	Glycerol monostearate	9
	Propyl parahydroxy benzoate	0.5
10	BHA + BHT	0.5

	<u>11 - Lipstick</u>	<u>% by weight</u>
	<u>White base :</u>	
	Petroleum ceresin	12
15	Candelilla wax	2
	Synthetic heavy esters (Croda Synchro wax ERLC - Croda is a Registered Trade Mark)	4
	Castor oil	10
	Blackcurrant oil	15
20	Isopropyl lanolate	15
	Liquid lanolin	10
	Acetylated lanolin	12
	Vaseline	10
	Cetyl ricinoleate	9.8
25	BHA + BHT (50/50)	0.2

to which are added 5.4 parts by weight of the

following pigments for 100 parts by weight of
white base :

Organic and mineral pigments:

	Red iron oxide	1.2
5	Titanium oxide	1.3
	D and C red No 9	2
	D and C red No 27	0.4
	Perfume	0.5

10 12 - Foundation (water-in-oil emulsion) % by weight

Oil phase:

	Liquid paraffin	5
	Blackcurrant oil	5
	Shorea fat	4
15	Perhydrosqualene	6
	Ozokerite	2
	Magnesium lanolate	5
	Lanolin alcohol	3
	Iron oxide	3
20	Titanium dioxide	4
	Polyethylene	10
	Perfume	0.4
	BHA + BHT	0.5

Water + preservative: quantity

5 sufficient for 100 %

	13 - <u>Baby bath oil</u>	<u>% by weight</u>
	Blackcurrant oil	20
	Oleic alcohol polyglycol ether	15
	Medium chain triglycerides(C ₈ -C ₁₀)	15
5	Isopropyl myristate	30
	Octyl palmitate	10
	Antioxidant (BHA + BHT) and perfume:	
	quantity sufficient for	100%

10 14 - Hair rinse % by weight

The following composition is prepared:

	Stearyl alcohol	1.8
	Cetylstearyl alcohol with 15 mols of E.O.*	5.6
	Blackcurrant oil	2.5
15	Quaternised cellulose sold under the name	
	JR 400 by Union Carbide	0.8
	Water quantity sufficient for	100.0

This composition is applied after the hair has been washed and is left on for 5 minutes. The hair is then rinsed. Wet hair is easy to comb out and the clean head of hair is soft and silky.

*Ethylene oxide

Examples 15 to 17 : dietetic foods

25	15 - <u>Dressing for salads</u>	<u>% by weight</u>
	Blackcurrant oil	10

20

	Grape pip oil	14.5
	White vinegar	3.2
	Red vinegar	4.4
	Mustard powder	5.35
5	Onion powder	0.25
	Salt	1.4
	Sugar	1
	Emulsifier	2.5
	Preservative (ascorbyl palmitate)	0.1
10	Powdered egg	4.2
	Water	53.1

	16 - <u>Oil for salads</u>	<u>% by weight</u>
	Blackcurrant oil	10
15	Grape pip oil	90

	17 - <u>Infant's milk</u>	<u>% by weight</u>
	Blackcurrant oil	0.61
20	(corresponds to 0.35 % of γ -linolenic acid calculated on the total weight of the fats, which is the amount in human milk)	} fats
	Corn oil	
25	Lactic fat	
	Medium chain triglycerides	
		2.47
		11.64
		9.28

	Carbohydrates, of which 41.6 of lactose and 15.3 of glucose	56.9
	Proteins, of which 4.4 of casein, and 10 of lactoserum proteins	14.4
5	Moisture	3.0
	Ash, of which :	1.7
	Calcium	350×10^{-3}
	Phosphorus	200×10^{-3}
	Potassium	370×10^{-3}
10	Sodium	103×10^{-3}

and the minimum quantities of the following vitamins
and trace elements:

15	Iron	6.0×10^{-3}
	Copper	0.3×10^{-3}
	Zinc	1.8×10^{-3}
	Iodine	25×10^{-6}
	Folic acid	80×10^{-6}
20	Vitamin C	200×10^{-3}
	Vitamin E	10×10^{-3}
	Vitamin B ₁	0.35×10^{-3}
	Vitamin B ₂	0.5×10^{-3}
	Vitamin B ₆	0.9×10^{-3}
25	Vitamin B ₁₂	1.7×10^{-3}
	Vitamin PP	5.2×10^{-3}

Calcium Pantothenate

2.6×10^{-3}

This powder is prepared as described in U.S. Patent
No. 4216236.

Examples 18 to 19 pharmaceutical compositions

5 18 - Capsules for oral administration

Gelatine capsules are prepared, containing 500 mg of
blackcurrant oil corresponding to 80 mg of γ -linolenic
acid per capsule.

10 19 - Fruit syrup for internal use % by weight

Blackcurrant oil 25

Mixture of mono- and diglycerides 2

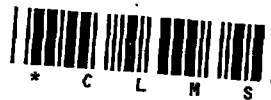
Mixture of gums 0.7

Sugar 17

15 Natural mixture of tocopherols

(α , β , γ and δ) 0.1

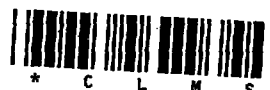
Preservative, flavourings and water;
quantity sufficient for 100 %



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CLAIMS

1. A nutritive composition (as herein defined) containing from 0.61 to 80% by weight of a fatty substance extracted from pips of fruits of the Ribes genus which fatty substance consists of triglycerides in which γ -linolenic acid represents at least 4% by weight of the fatty acids and, which is substantially free from the odorous compounds, the free fatty acids the colourings and the waxes naturally present in the oil of the pips of fruits of the Ribes genus.
2. A nutritive composition according to claim 1, wherein the fatty substance is blackcurrant oil.
3. A composition as claimed in claim 1, which is an aqueous or anhydrous cosmetic or dermatological composition containing an oil phase, wherein the oil phase contains from 1 to 80% by weight, based on the total weight of the oil phase, of the fatty substance extracted from pips of fruits of the Ribes genus.
4. A composition as claimed in claim 1, which is a dietetic food or food supplement comprising a fatty material; wherein the fatty material comprises from 0.61 to 15% by weight of the fatty substance extracted from pips of fruits of the Ribes genus.
5. A composition as claimed in claim 1, which is a pharmaceutical composition containing from 5 to 80% by weight of the fatty substance extracted from pips of fruits of the Ribes genus, in a form adapted for topical, oral, enteral or parenteral administration.
6. A process for the preparation of fatty substances



from pips of fruits of the Ribes genus, in which a vegetable material containing such pips is ground and extracted with a solvent in order to obtain a fatty substance which consists of triglycerides in which γ -linolenic acid represents at least 4% by weight of the fatty acids and which is substantially free from the odorous compounds, the free fatty acids, the colourings and the waxes naturally present in the oil of the pips of fruits of the Ribes genus.

7. A process as claimed in claim 6, wherein the vegetable material which is used comprises residues from the production of juices, jellies, or preserves, brandies, liqueurs, or schnapps of blackcurrants, redcurrants, gooseberries, hybrids or mixtures of these fruits.

8. A process as claimed in claim 6 or 7, wherein the vegetable material which has been previously dried is ground, the ground vegetable material is washed with a solvent or a supercritical fluid in a polar condition in order to remove the waxes, most of the colouring materials and the free fatty acids, naturally present in the oil of the pips of fruits of the Ribes genus, the material is drained, the residue is finely ground, moistened and made into granules or pellets, extracted with a non-polar solvent or a supercritical fluid in a slightly polar condition and the latter is removed by evaporation.

9. A process as claimed in claim 6 or 7, wherein the vegetable material which has been previously



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dried is ground, the ground vegetable material is washed with a polar solvent or a supercritical fluid in a polar condition in order to remove the waxes, most of the colouring materials and the free fatty acids naturally present in the oil of the pips of fruits of the Ribes genus, the material is drained, the drained residue is subjected to a sieving operation and an elutriation operation so that it essentially comprises pips of from 1 to 1.5 mm, and the pips are made into flakes, the flakes are extracted with a non-polar solvent or a supercritical fluid in a slightly polar condition and the latter is removed by evaporation.

10. A process as claimed in claim 8 or 9, wherein the ground vegetable material is washed with ethanol under reflux.

15 11. A process as claimed in claim 8 or 9, wherein the ground vegetable material is washed with supercritical carbon dioxide in a polar condition under a pressure of above 250 bars and at a temperature of from 60 to 80°C.

20 12. A process as claimed in claim 8 or 9, wherein the washed residue is extracted with hexane under reflux.

13. A process as claimed in claim 8 or 9, wherein the washed residue is extracted with supercritical carbon dioxide in a slightly polar condition under a pressure of from 200 to 300 bars and at a temperature of from 40 to 60°C.



14. A process as claimed in claim 8, wherein after the residue has been extracted, the non-polar solvent is partially evaporated until a solution containing from 80 to 90% by weight of solvent is obtained, the solution is neutralized with a concentrated alkali, is maintained at a temperature of from 0 to 4°C for about 24 hours, is filtered, and the solvent is removed by evaporation.

15. A process as claimed in claim 14, wherein after the residue has been extracted, the solvent has been partially evaporated and the solution has been neutralized, the solution is decolorized using from 2 to 8% of active carbon based on the weight of the fatty substance in solution.

16. A process as claimed in claim 14 or 15, wherein after the solvent has been evaporated, the oil is deodorized at a temperature of from 140 to 220°C and under a vacuum of less than 1 torr.

17. A process as claimed in claim 8, wherein the vegetable material which has been previously dried is ground and sieved, made into flakes or finely ground, moistened and made into granules or pellets, extracted with a non-polar solvent, the solvent is partially evaporated until a solution containing from 80 to 90% by weight of solvent is obtained, the solution is neutralized with concentrated sodium or potassium



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hydroxide, is maintained at a temperature of 0 to 4°C for about 24 hours, filtered, decolorized with from 2 to 8% of active carbon based on the weight of the oil in solution, the solvent is evaporated and the oil is
5 deodorized at a temperature of from 140 to 220°C and under a vacuum of less than 1 torr.

18. A process as claimed in claim 17, wherein the oil which is obtained is saponified with an alkali metal hydroxide in a water-alcohol medium, the
10 resulting salts are acidified with a concentrated mineral acid, the free fatty acids naturally present in the oil of the pips of fruits of the Ribes genus are extracted by the addition of a non-polar solvent, by separating and drying the organic phase and a fraction concentrated in γ -linolenic acid is separated by high performance
15 chromatography in liquid phase over a silica gel column charged with silver cations by an isocratic method.

19. A process as claimed in claim 8, wherein the moist, ground vegetable material is treated with an alkali metal hydroxide, the suspension is acidified
20 with a concentrated mineral acid, the free fatty acids naturally present in the oil of the pips of fruits of the Ribes genus, are extracted by the addition of a non-polar solvent, by separating and drying the organic phase, and a fraction concentrated in γ -linolenic acid is separated by high performance chromatography in liquid phase over a
25 silica gel column charged with silver nitrate by an isocratic method.



20. A process as claimed in claim 18 or 19,
wherein by using high performance liquid phase chromatogra-
phy with a C₈ or C₁₈ support in reversed phase and by
using a solvent gradient, a fraction essentially con-
5 taining γ -linolenic acid is eluted.

21. Fatty substances from pips of fruits of the
Ribes genus when extracted by a process as claimed in any
of claims 6 to 20.

22. A nutritive composition (as herein defined) containing fatty
10 substance extracted from pips of fruits of the Ribes
genus substantially as described with particular
reference to any of Examples 4 to 19.

23. A process for the preparation of fatty
substances from pips of fruits of the Ribes genus
15 substantially as described with particular reference to
any of Examples 1 to 3.
