(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 December 2003 (11.12.2003)

PCT

(10) International Publication Number
WO 03/102072 A1

(51) International Patent Classification[7]: C08L 3/02, C08B 30/00, 30/12, 31/00, A21D 13/06, A23B 9/16, 9/24, 9/26, A23C 9/13, 9/137, 9/152, 9/154, A23D 7/06, A23L 1/0522, 1/10, C11B 5/00

(21) International Application Number: PCT/NZ03/00114

(22) International Filing Date: 30 May 2003 (30.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
519279 30 May 2002 (30.05.2002) NZ

(71) Applicants *(for all designated States except US)*: **GRANATE SEED LIMITED** [NZ/NZ]; Level 1, 24 Johnston Street, Wellington (NZ). **INDUSTRIAL RESEARCH LIMITED** [NZ/NZ]; Brooke House, 24 Balfour Road, Parnell, AUCKLAND (NZ).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **MORGAN, Keith, Raymond** [NZ/NZ]; 6 Oriental Street, Petone, LOWER HUTT (NZ).

(74) Agent: **BALDWIN SHELSTON WATERS**; Level 16, HSBC House, 1 Queen Street, AUCKLAND (NZ).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/102072 A1

(54) Title: STARCH PRODUCTS INVOLVING A STARCH-LIPID COMPLEX, THEIR PREPARATION AND USES

(57) Abstract: A starch product which contains up to approximately 10% by weight lipid associated with the starch in the starch product and where less than approximately 50% by weight of the starch in the starch product has been gelatinised. In addition, starch products in which lipids are stabilised from decomposition, including air oxidation are provided. Methods for the production of starch products of the invention, and uses for such starch products are also provided.

STARCH PRODUCTS INVOLVING A STARCH-LIPID COMPLEX, THEIR PREPARETION AND USES

FIELD

This invention relates to novel products formed by reacting starch with lipids. The invention also relates to processes for the preparation of such products and uses of the products. In particular, the invention relates to starch products where the granular structure of the starch is essentially retained and/or to starch products where the lipids are protected from decomposition.

BACKGROUND

Starch granules are comprised of two polysaccharides, amylose and amylopectin. Both polysaccharides are comprised of 4-linked D-glucopyranosyl units. Amylose is a linear molecule, whereas amylopectin is highly branched since some 5-6 % of the 4-linked units are also 6-linked. Starch occurs in a wide variety of plants including cereals and tubers such as potato. Starch granules isolated from cereals contain lipids which are complexed mainly to the amylose.

Starch is isolated on a commercial scale from tuber and cereal crops including potato, maize, and wheat. It is used extensively in processed foods and has many industrial uses, such as a paper coating. The starch may be modified to alter its chemical or physical properties before use.

The known methods for modifying starch include chemical derivatisation, gelatinisation and enzymatic modification. Recently there has been interest in modifying starch by adding lipids during hydrothermal treatment of the starch. The starch is gelatinised in the presence of the lipid so that a certain amount of the lipid associates with the starch to form a type of starch-lipid complex.

Starch is used in a multitude of industrial applications. It is prevalent in the processed foods industry as a food additive, particularly in dairy foods but also many others. Starch is also an important component of many pharmaceutical formulations.

Starch obtained from natural sources has a granular structure as indicated above. However, the starch that is used in some industrial applications has undergone gelatinisation where starch granules alter their structure, usually in response to heating in

the presence of water. Amylopectin in starch granules is comprised of alternating amorphous and crystalline regions. These crystalline regions melt during gelatinisation.

In some applications using starch, granular starch is preferred whereas in other applications pre-gelatinised starch is preferred. Even where there is no preference for the physical form of the starch used, avoiding gelatinisation of the starch has the processing advantage that a costly step of removal of water is avoided. Gelatinised starch has a significant amount of water associated with it, but many applications require the removal of that water before use. It is therefore desirable to prepare starch products (starch-lipid complexes) where gelatinisation of the starch is avoided.

In nature, most lipids are oils and fats composed of triglycerides. Triglycerides are fatty acid esters of glycerol in which all three hydroxyl groups are esterified with fatty acids. However, lipids that are associated with starch are mainly free fatty acids and phospholipids containing a single fatty acid residue.

Lipids occur widely in nature and can be isolated from both plants and animals. For human nutrition there are lipids that are considered essential. These are lipids that the human animal cannot synthesise *in vivo*. It is the fatty acid residue of a lipid that is the essential component for healthy nutrition. There are two classes of these essential fatty acids which are both polyunsaturated. One class is the omega-6 fatty acids which have their first double bond from the methyl end of the fatty acid at carbon atom number 6 and the second class is the omega-3 fatty acids which have their first double bond from the methyl end of the fatty acid at carbon atom number 3. The average western diet is considered to be deficient in intake of omega-3 fatty acids.

There are three main dietary sources for omega-3 fatty acids: α-linolenic acid obtained from plants, and eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) both present in marine organisms. It is thought that α-linolenic acid can to some extent be desaturated and elongated during metabolism in humans to form EPA and DHA.

Reduced dietary intake of omega-3 fatty acids is thought to be a risk factor in coronary heart disease, to predispose one to depression, and to have other adverse health effects.

A problem in providing essential fatty acids for human nutrition is that polyunsaturated fatty acid residues in oils and fats are less stable than oils and fats containing saturated

fatty acid residues. Polyunsaturated fatty acids in particular can be readily oxidised by oxygen in the air. Usually, the more unsaturated the fatty acid, the less stable it will be. EPA and DHA are especially susceptible to air oxidation and can oxidise up to five times faster in air than linoleic acid. The incorporation of oils containing EPA and DHA into processed foods can therefore be problematic. Such foods can quickly become rancid due to oxidisation. Moreover oxidised polyunsaturated fatty acids are considered to be toxic. Essential fatty acid residues are no longer available to the human animal once oxidised.

Polyunsaturated fatty acids in fats and oils have traditionally been stabilised by the addition of antioxidants. However, once all the antioxidant has been oxidised the polyunsaturated fatty acids can then undergo a rapid auto-oxidation process. Also, there is some disadvantage to adding antioxidants since they are often not naturally occurring in foods.

The applicant has now found a novel starch product which can be prepared without any significant gelatinisation of the starch and a novel starch product which protects an otherwise susceptible lipid from air oxidation.

It is therefore an object of the invention to provide a starch product and a process for preparing it, or to at least provide a useful alternative to known starch products and processes for forming them.

STATEMENTS OF INVENTION

In one aspect of the invention there is provided a starch product which contains up to approximately 10 % by weight lipid associated with starch in the starch product and where less than approximately 50 % by weight of the starch in the starch product has been gelatinised.

In a preferred embodiment the starch product contains 0.5 to 2 % by weight lipid in the starch product.

Preferably less than approximately 10 % by weight of the starch in the starch product has been gelatinised, more preferably less than approximately 5 %.

The lipid may be any free fatty acid or any fatty acid derivative such as an ester of a fatty acid, or may be any combination or mixture thereof. The ester of a fatty acid is preferably a monoglyceride or a phospholipid.

Preferably, the lipid present within the starch product is stabilised to decomposition. More preferably, the lipid is stabilised to air oxidation.

In a second aspect of this invention there is provided a process for preparing the starch product of the first aspect of this invention including the steps:

a) contacting an aqueous solution or emulsion of the lipid, or a salt of the lipid, with starch to form a mixture of the starch and the lipid; and
b) where the ratio of water to starch in the mixture is above approximately 50 % by weight, heating the mixture to form the starch product at a temperature below the gelatinisation temperature of the starch; or
c) where the ratio or water to starch in the mixture is below approximately 50 % by weight, heating the mixture to form the starch product at a temperature either above or below the gelatinisation temperature of the starch.

In a third aspect of the invention there is provided a starch product which contains one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives, where the starch product contains up to approximately 30% by weight of the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives in the starch product, and where the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives associate with the starch so that the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives are stabilised to decomposition.

In a preferred aspect of the invention the starch product contains up to approximately 10 % by weight of one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives.

In another preferred aspect of the invention the starch product contains less than approximately 5 % by weight of one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives.

In one preferred aspect of the invention the starch product contains less than approximately10 % by weight of a derivative of a polyunsaturated fatty acid.

Preferably the one or more polyunsaturated fatty acid derivatives mentioned in the third aspect includes an ester of a polyunsaturated fatty acid, for example a monoglyceride or a phospholipid.

In a preferred embodiment of the invention the one or more polyunsaturated fatty acids includes an omega-3 fatty acid, such as α-linolenic acid, eicosapentaenoic acid (EPA) or docosahexaenoic acid (DHA).

Preferably the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives are stabilised to air oxidation.

In a fourth aspect, the invention provides a starch product which contains one or more omega-3 fatty acids and/or derivatives of omega-3 fatty acids, where the starch product contains up to approximately 10 % by weight of the one or more omega-3 fatty acids or derivatives thereof.

In a fifth aspect, the invention provides a starch product which contains one or more salts of polyunsaturated fatty acids, where the starch product contains up to approximately 30 % by weight of one or more polyunsaturated fatty acids.

The starch product of the third to fifth aspects of the invention may be prepared in a similar manner to the method of the second aspect, although it is not necessary to avoid gelatinisation in the heating step. Preferably, the starch products of the third to fifth aspects are prepared by a process including at least the steps of:

a) contacting an aqueous solution or emulsion of the polyunsaturated fatty acid, and/or polyunsaturated fatty acid derivative, with starch to form a mixture of the starch and the polyunsaturated fatty acid or derivative; and
b) heating the mixture to a temperature above the gelatinisation temperature of the starch in the presence of water at greater than approximately 50% by weight of the starch.

Preferably, water is present at greater than approximately 100% by weight of the starch.

The starch used in any aspect of the invention is preferably used in the form in which it occurs naturally, for example solid potato or cereal grain, including their processed forms such as flour. In another preferred form, the starch may be in purified form such as

purified starch isolated from cereal grain, or an enzymatic or chemical derivative of the starch.

If a starch product of the invention contains free fatty acids the product may be either in its acidic or basic form.

In a further aspect of the invention there is provided the use of a starch product of this invention in a food or as a food.

In another aspect, the invention provides a food comprising at least a starch product of the invention.

The invention also provides a food incorporating one or more lipids and/or salts thereof wherein the one or more lipids or salts thereof are present in the form of a starch product of the invention. Preferably, the food incorporates one or more polyunsaturated fatty acids or derivatives thereof in the form of a starch product of the invention.

In a further aspect, the invention provides a pharmaceutical comprising at least a starch product of the invention, optionally in association with one or more pharmaceutically acceptable carriers, diluents, and/or excipients.

In yet a further aspect of the invention there is provided the use of starch for the stabilisation of one or more lipids or salts thereof by adding the one or more lipids or salts thereof to starch. More preferably, the invention provides the use of starch for the stabilisation of one or more polyunsaturated fatty acids and/or derivatives thereof by adding the one or more polyunsaturated fatty acids and/or derivatives thereof to starch.

Preferably the starch is present in, or is added to, a food or a pharmaceutical.

In another aspect, the invention provides a starch product produced by a process of the invention.

In yet a further aspect, the invention provides a process for making a food product comprising the step of preparing a starch product of the invention.

In another aspect, the invention provides the use of a starch product of the invention in the manufacture of a medicament for the prevention and/or amelioration of depression and/or coronary heart disease.

Further, the invention provides a starch-containing processed food in which starch is associated with one or more polyunsaturated fatty acids and wherein the one or more polyunsaturated fatty acids are stabilised to decomposition.

In addition there is provided a process of making a starch-containing processed food the method comprising at least the step of adding one or more polyunsaturated fatty acids and/or their derivatives to one or more ingredients of the food during processing. Starch-containing processed foods obtained by this process are a further aspect of the invention.

The invention also provides starch-containing processed foods in which starch is associated with one or more polyunsaturated fatty acids and/or their derivatives, particularly one or more omega-3 fatty acids and/or their derivatives.

Other aspects of the invention may become apparent from the detailed description and examples provided herein after.

DETAILED DESCRIPTION

The present invention involves the association between lipids and starch. The applicant has shown that this association has the effect of protecting the fatty acids, particularly polyunsaturated fatty acids, from decomposition, including protection from air oxidation. The applicant has also demonstrated starch products containing lipids and methods of producing same wherein less than approximately 50% by weight of starch present in the product has been gelatinised. The benefits associated with stabilising fatty acids and/or reducing gelatinisation of starch will be readily appreciated by skilled persons.

The following is a description of the invention, including preferred embodiments thereof, given in general terms. The invention is further elucidated from the "Examples" provided herein after.

As used herein, "decomposition" refers to any chemical alteration of the lipid and includes that which may occur via cross-linking or oxidation.

For the purpose of this invention "lipid" is defined as including long chain (>C-6) carboxylic acids and their monoesters such as monoglycerides or phospholipids, but not di- or tri-glycerides or other di- and tri-esters.

"Polyunsaturated fatty acids" as referred to herein are fatty acids having two or more double bonds and may be considered a subset of the lipids described in the paragraph above.

It should be appreciated that the invention is applicable to salts of lipids and derivatives of polyunsaturated fatty acids. Accordingly, it should be appreciated that when used in relation to the invention the terms "lipid" and "polyunsaturated fatty acid" can be taken to include reference to their salts and derivatives, respectively.

As used herein, "derivatives of polyunsaturated fatty acids" includes salts, and esters such as monoglycerides or phospholipids. Skilled persons will readily appreciate salts of fatty acids of use in the invention. Specific examples are provided herein after in the section entitled "Examples". Further examples include potassium salts.

Where referred to herein, the association between a lipid and starch in the starch product of this invention is intended to mean a molecular association between the lipid and predominantly the amylose in the starch granules. Strongly associated lipids are not washed out of the starch product of this invention by a solution of 0.01 M NaOH. Weakly associated lipids may be washed out, but nevertheless stabilised to air oxidation by association with the starch.

In one embodiment the invention provides a starch product which contains up to approximately 10 % by weight lipid, more preferably 0.5 to 2% by weight lipid, associated with starch. Less than approximately 50 % by weight of the starch in the product has been gelatinised. In particularly preferred embodiments less than approximately 10%, and more preferably less than approximately 5%, by weight of the starch in the product has been gelatinised.

Starch products of this embodiment of the invention may be made by a process which includes at least the steps:

a) contacting an aqueous solution or emulsion of the lipid, or a salt of the lipid, with starch to form a mixture of the starch and the lipid; and

c) where the ratio of water to starch in the mixture is above approximately 50 % by weight, heating the mixture to form the starch product at a temperature below the gelatinisation temperature of the starch; or

d) where the ratio or water to starch in the mixture is below approximately 50 % by weight, heating the mixture to form the starch product at a temperature either above or below the gelatinisation temperature of the starch.

Persons of general skill in the art will readily appreciate protocols for conducting the above process having regard to the nature of the lipid and starch being used. However, by way of general example, in a typical reaction procedure a lipid is dissolved in water or an emulsion of the lipid with water is formed. The solution or emulsion is then mixed with starch. If the water content is greater than about 50 % by weight of the starch content, the reaction temperature should be kept below about 55 °C to avoid starch gelatinisation. Elevated reaction temperatures (greater than about 60 °C) can be used if the water content is below about 50 % by weight of the starch. Flour containing starch can be treated in a similar manner. Specific examples of making a starch product of this embodiment of the invention are provided herein after under the heading "Examples"; see Examples 1 to 11.

In another embodiment, the invention relates to a starch product which contains one or more polyunsaturated fatty acids or polyunsaturated fatty acid derivatives, where the starch product contains up to approximately 30% by weight, preferably up to approximately 10% by weight, of the one or more unsaturated fatty acids or unsaturated fatty acid derivatives. In a preferred form, the product contains less than approximately 5% by weight of one or more polyunsaturated fatty acids or their derivatives. The one or more polyunsaturated fatty acids or polyunsaturated fatty acid derivatives in the product associate with the starch so that they are stabilised to decomposition, particularly air oxidation.

The inventor has found that for a typical cereal or tuber starch, up to about 30% by weight of the polyunsaturated fatty acids can associate with the starch to stabilise them to decomposition. For derivatives of polyunsaturated fatty acids the inventor notes that up to approximately 10% by weight can generally associate with the starch to be stabilised to decomposition. However, the inventor contemplates the invention being applicable to starch products containing in excess of 10% derivatives of polyunsaturated fatty acids.

This embodiment of the invention may be applicable to any number of polyunsaturated fatty acids or their derivatives. However, the inventor has identified it to be particularly applicable to omega-6 fatty acids and also omega-3 fatty acids, such as, α-linolenic acid, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA).

In a particularly preferred embodiment of the invention the starch product contains up to approximately 10% by weight of one or more omega-3 fatty acids or derivatives of omega-3 fatty acids.

The starch products of this embodiment of the invention may be prepared by any number of reaction procedures. Generally, they may be prepared in a similar manner to the method described herein above, although it is not necessary to avoid gelatinisation in the heating step. By way of general example, the process may include at least the steps of:

a) contacting an aqueous solution or emulsion of the polyunsaturated fatty acid, or polyunsaturated fatty acid derivative, with starch to form a mixture of the starch and the polyunsaturated fatty acid or derivative; and
b) heating the mixture to a temperature above the gelatinisation temperature of the starch in the presence of water at greater than approximately 50% by weight of the starch.

Preferably, water is present at greater than approximately 100% by weight of the starch.

For polyunsaturated lipids or other therapeutic agents that are stabilised by association with starch in accordance with this embodiment of the invention it is preferred that the lipid be incorporated into a food by cooking or heating and/or gelatinising a starchy material, such as a cereal flour, in the presence of the lipid. For example, the lipids may be added to starchy processed foods such as bread during formation of the products. In bread baking, a polyunsaturated fatty acid or derivative can be added as an ingredient to the flour or if preferred mixed with water which is then added to the flour during mixing to form a dough. Skilled persons will readily appreciate other starch-containing processed foods applicable to the invention.

Alternatively, starch can be pre-treated with a polyunsaturated fatty acid or derivative to form a starch product, which may then be added to a food product. The starch product can be formed by gelatinisation of the starch in the presence of a polyunsaturated fatty

acid or derivative and then dried, or the starch product may be formed as described above for the first aspect of this invention.

The starch used in the invention may be in a purified form. For example, purified starch isolated from cereal grain, native corn, maize or wheat flour may be used. In addition the starch may be an enzymatic or chemical derivative of starch isolated from such sources. However, the starch used need not be separated and purified from its "source material" and may be used in the form in which it naturally occurs. The source material itself, for example a solid potato or other tuber, or cereal grain, can be heated at appropriate temperatures having regard to the abovementioned starch products and methods of the invention.

As used herein "source material" is intended to include processed forms of a raw material. For example, in the case of cereal grain, flour may be used.

The starch gelatinisation temperature, which may be referred to herein, depends to an extent on the form of starch used and its origin, but is typically in the range 50 to 80 °C. Skilled persons will readily appreciate gelatinisation temperatures having regard to the form of starch used and its origin without undue experiment.

It should be appreciated that the starch products of the invention may contain a single type of lipid or salt thereof (including polyunsaturated fatty acids and their derivatives) or a combination of two or more different types thereof. In addition, the starch product may include an emulsion of one or more such lipids or their salts.

In addition, two or more different types of starch or sources of starch may be used in a single product of the invention.

Where lipids in a starch product of the invention are free fatty acids their carboxylic acid group may be ionised. Accordingly, in this form the product may be in an acidic form or a basic form.

The starch products of the invention may have a variety of uses. For example, they may be used in a food or as a food. Another embodiment of the invention is a food incorporating one or more lipids in accordance with the invention. The starch products of the invention may also be used as or in pharmaceuticals.

Examples of food products to which this invention is applicable include bread, pasta, baked goods, or any starch containing processed food. The food product may be prepared by simply adding a starch product of the invention at an appropriate time during preparing of the food. Alternatively, the starch product may be formed in the process of preparing the food product (as mentioned herein before).

The starch products of the invention may be used pharmaceutically, alone or in combination with suitable active ingredients and/or pharmaceutically acceptable diluents, carriers and/or excipients as are generally known. Having the starch products of the invention to hand, appropriate pharmaceuticals may be formulated into standard dosage forms (for example capsules and tablets), by combining with various actives and/or excipients, carriers or diluents, in accordance with standard methodology.

In a further embodiment, starch products as herein described may be used in the manufacture of medicaments for the prevention and/or amelioration of depression and/or coronary heart disease. This is particularly applicable where omega-3 fatty acids are contained within the starch product.

EXAMPLES

The invention is described with reference to the following examples. However, it is to be appreciated that the invention is not be limited to any of the examples.

Example 1

Sodium oleate (300 µL, 10 wt % in water) was mixed with maize starch (1.0 g) at 80 °C for 64 h. The annealed starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH, followed by drying. The starch was recovered between washings by centrifugation. The amount of strongly associated lipid was determined to be 1.7 % by weight of starch using a pH titration with HCl (0.001 M).

Example 2

An emulsion (300 µL) of sodium oleate (10 wt %) and oleic acid (5 wt %) in water was mixed with maize starch (1.0 g) at 80 °C for 64 h. The annealed starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out the NaOH, followed by drying.

The starch was recovered between washings by centrifugation. The amount of strongly associated lipid was determined to be about 1.9 % by weight of starch using a pH titration with HCl (0.001 M).

Example 3

Sodium oleate (300 µL, 10 wt % in water) was mixed with maize starch (1.0 g) and water (700 µL) at 65 °C for 64 h. The annealed starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out the base. The starch was recovered between washings by centrifugation. The amount of strongly associated lipid was determined to be about 1.6 % by weight of starch using a pH titration with HCl (0.001 M). Similar results were obtained for reaction of an emulsion of sodium oleate (300 µL, 10 wt %) and oleic acid (5 wt %) in water with starch at 65 °C.

Example 4

Samples of maize and potato starch (1.0 g) were separately reacted with a lipid mixture containing 70 % sodium linoleate (200 µL, 10 wt % in water) and water (100 µL) at 80 °C for 17 h. The annealed starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH. The starch was recovered between washings by centrifugation. The amount of strongly associated lipid was determined to be about 1.3 % by weight of starch in both starch products using a pH titration with HCl (0.001 M).

Example 5

Samples of maize and potato starch (1.0 g) were separately mixed with an aqueous solution containing 70 % sodium linoleate (300 µL, 10 wt % in water) and water (100 µL) at 30 °C for 16 h. The treated starches were then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH, followed by drying. The starch was recovered between washings by centrifugation. The amount of strongly associated lipid was determined to be 1.0 % by weight for the maize starch and 0.7 % by weight for the potato starch using a pH titration with HCl (0.001 M).

Example 6

Samples of maize and potato starch (1.0 g) were separately reacted with sodium oleate (300 µL, 10 wt % in water) at 95 °C for 0.5 h. The treated starch was then washed with

NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH, followed by drying. The starch was recovered between washings by centrifugation. The amount of strongly associated lipid was determined using a pH titration with HCl (0.001 M). It was found that about 1.1 % by weight of oleate was associated with the corn starch and 1.4 % by weight with the potato starch.

Example 7

Samples of maize and potato starch (1.0 g) were separately reacted with sodium oleate (200 µL, 10 wt % in water) and water (200 µL) at 50 °C and also at 30 °C for 92 h. The treated starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH, followed by drying. The amount of strongly associated lipid was determined using a pH titration with HCl (0.001 M). For treatment at 30 °C it was found that 0.90 % and 1.3 % by weight of oleate was associated with the maize and potato starch respectively and for treatment at 50 °C the values were 1.1 and 1.4 % by weight respectively.

Example 8

Samples of sodium oleate (200 µL, 10 wt % in water) were reacted with maize starch samples (1.0 g) and water (100 µL) at 95 °C for 1, 2, 4, and 24 h. The annealed starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH. The starch was recovered between washings by centrifugation. The amount of associated lipid was determined by a pH titration with HCl (0.001 M). The amount of lipid strongly associated with the starch for each reaction time is shown in Table 1. This shows that the lipid association with starch occurs over a period of a few hours.

Table 1

Reaction time/h	*Lipid wt% associated*
1	1.12
2	1.33
4	1.37
24	1.3

Example 9

Solutions of sodium oleate (200 µL, 10 wt % in water) together various amounts of additional water according to Table 2 were mixed with samples of maize starch (1.0 g) at 95 °C for 2 h. The annealed starch was then washed with NaOH (40 ml, 0.01 M) to remove lipid that was not strongly associated with the starch, followed by three lots of ultrapure water to wash out NaOH, followed by drying. The starch was recovered between washings by centrifugation. With the addition of 500 µL of water it was noted that the starch was partially gelatinised. The amount of strongly associated lipid was determined using a pH titration with HCl (0.001 M), and the variation for different amounts of water used in the reaction is shown in Table 2. Thus water content appears to have little effect on lipid association.

Table 2

Water/µL	*Lipid %w associated*
200	1.2
300	1.3
400	1.3
500	1.3

Example 10

Maize starch in water was gelatinised at 95 °C for 10 min. The solution was cooled and a pullulanase (10 µL, Novo Nordisk) was added and the mixture allowed to react for 12 h. The starch was then heated with sodium linoleate solution (357 µL, 0.5 M) at 95 °C for 10 min. A soft gel formed on cooling.

Example 11

Oleic acid (100 mg) was dissolved in NaOH solution (3.56 ml, 0.1 M) at 50 °C. Starch was added to the solution and dispersed by shaking. The solution was then heated on a boiling water bath for 10 min to gelatinise the starch. The gelatinised starch was washed with ultrapure water three times and the gelatinised starch recovered between washings by centrifugation. Water was removed from the gelatinised starch by washing with

ethanol. The starch was recovered by filtration and dried. The amount of strongly associated lipid was determined to be 1.4 % by weight of starch using a pH titration with HCl (0.001 M).

Example 12

Free fatty acids containing approximately 62 % linolenic acid were prepared by stirring rapidly pure cold-pressed linseed oil (37 g), with sodium hydroxide (5.1 g) in water (16 ml) and ethanol (42 ml). After 3 h reactions the ethanol was removed from the solution on a rotary evaporator. The oily solution was neutralised with HCl and washed several times with water to yield the free fatty acids.

Sodium Linolenate (62 % purity) was formed by neutralising the free fatty acids with 1 mol equivalent of sodium hydroxide in ethanol.

The following examples may involve measuring oxidation of lipids. Unless otherwise indicated, measurement of oxidation was conducted as follows:

Oxidation of lipids was followed by measuring pressure changes in a sealed tube as oxygen was consumed during oxidation of the lipid. The tube having a volume of approximately 8.5 ml was placed in a water bath which was heated on a hotplate stirrer at 50 °C. Temperature regulation of the water bath was ±0.3 °C. Contents in the tube were stirred by means of a teflon-coated magnetic stirring bar. The water bath was wrapped in aluminium foil to exclude light falling on the tube. Absolute pressure changes in the tube was followed by measuring changes in the voltage of a pressure transducer (PX137-015AV, Omega Engineering) placed above the water bath and attached to the tube by a silicone sealing glue. Correction to the pressure of 2 hPa/°C were made to account for changes in room temperature, which effects the voltage of the transducer.

Pressure changes as small as ± 2 hPa could be followed. Since oxygen comprises about 21 % of gases in the atmosphere changes of about 200 hPa indicate complete consumption of the oxygen in the oxidation reaction.

Example 13

A lipid mixture containing 70 % by weight linoleic acid (50 mg) dissolved in NaOH (1.8 ml, 0.1 M) was mixed with maize starch (5 g) and reacted at 95 °C for 2 h. The annealed

starch was then washed with NaOH (40 ml, 0.01 M) to remove unassociated lipid followed by three lots of ultrapure water to wash out NaOH, followed by drying. The annealed starch (4 g) was stirred with water (5 ml) in a Warburg apparatus at 50 °C. Over the course of the experiment (46 h) no oxygen uptake occurred. In comparison, with the lipid mixture containing 70 % by weight linoleic acid (40 mg) in NaOH (1.8 ml, 0.1 M) and water (3.2 ml), oxidation was rapid and off-scale within 10 h.

Example 14

A lipid mixture containing 70 % by weight sodium linoleate solution (600 µL, 0.5 M) was mixed with maize starch (5 g) in a mortal and pestle. The lipid level was calculated to be 4.2 wt % of the starch. The mixture was placed in a Warburg apparatus at 50 °C. Over the course of the experiment (120 h) there was no significant oxygen uptake within the first 60 h and only a small amount of oxygen uptake in the following 60 h. Previous experiments suggest that not more than about 1.5 % by weight of the lipid was strongly associated with the starch, but in this experiment 4.2 w% of the lipid appears to be stabilised to air oxidation by association with the starch polysaccharides.

With the lipid mixture containing 70 % by weight linoleic acid (40 mg) in NaOH (1.8 ml, 0.1 M) and water (3.2 ml) with no starch, oxidation in the Warburg apparatus at 50 °C was rapid and off-scale within 10 h.

Example 15

Sodium linolenate (35 mg) was mixed with various quantities of corn starch and water (4.5 ml) and the oxidation of the lipid recorded in the apparatus described above. With no starch present oxidation is rapid with most of the oxygen being consumed within 25 h. With starch (0.75 g) present no oxidation of the lipid occurs within 25 h. Even with just a small amount of starch (0.095 g) in the oxidation apparatus, only 7.5 % of the oxygen in the vessel has been consumed after 40 h reactions. For the last case the weight percent of lipid to starch is 37 %. Thus it appears that only relatively small amounts of starch are required to give stability to the linolenate.

Example 16

The oxidation of sodium linolenate was determined in the presence of equivalent weights of one of the following: corn starch, maltose or a maltooligosaccharide. The starch was found to completely inhibit the oxidation of the linolenate. With the maltooligosaccharides 20% of the oxygen was consumed after 20 h, whereas for the maltose 40 % of the oxygen

was consumed. Thus starch shows the greatest efficacy for inhibiting oxidation of sodium linolenate.

Example 17

Starch (0.3 g) was mixed with a solution of sodium linolenate (1 ml, 0.1 M) and then dried in a vacuum desiccator. The oxidation of the dried starch/sodium linolenate mixture was compared to a solution of sodium linolenate (1 ml, 0.1 M). For the solution oxidation was rapid. Most of the oxygen had been consumed within 30 h. However, for the dried starch/sodium linolenate mixture only a small amount of oxidation had occurred after 30 h.

Example 18

Sodium linolenate (34 mg) was mixed with starch (0.2 g) in water (4.5 ml) and the oxidation of the sodium linolenate was determined in the apparatus described above. For both waxy and high amylose starches no significant amount of oxidation occurred after 45 h of reaction.

Example 19

An emulsion (37 mg) of sodium linolenate (66 %) and linolenic acid (33 %)
was mixed with starch in water (4.6 ml). Oxidation was determined in the apparatus described above. With no starch present in the reaction medium most of the oxygen had been consumed after 60 h. With starch (0.1 g) present only 20 % of the oxygen had been consumed after 60 h.

Example 20

Starch (1 g) was gelatinised with a mixture of lipids containing 80 % monoglycerides of linseed oil (20 mg) and water (0.66 g) for 1 h at 95 °C for 1 h. The starch product was dried under vacuum and ground to a powder in a mortar and pestle. In the oxidation apparatus described above a mixture of this starch product in water (2.6 ml) showed little or no reaction with oxygen after 30 h. For comparison, the 80 % monoglyceride mixture of linseed oil (20 mg) in water (3.6 ml) consumed most of the oxygen in the reaction vessel after 30 h.

Example 21

Starch (1.7 g) was gelatinised with a lipid mixture containing 80 % monoglycerides of linseed oil (25 mg) and water (0.85 ml). The starch product was dried under vacuum and ground to a powder in a mortar and pestle. The dried powder was placed in the oxidation

apparatus described above. Some oxygen absorption was observed after 24 h. After 100 h no further oxygen absorption was observed. In total 100 hPa of oxygen had been absorbed. The amount absorbed is consistent with the presence of diglycerides present in the lipids, which were not expected to react with the starch and therefore not to be stabilised. In contrast for the lipid mixture (25 mg) in the apparatus without any starch most of the oxygen (200 hPa) was consumed after 25 h reaction.

Although the invention has been described by way of example, it should be appreciated that variations and modifications may be made without departing from the scope of the invention. Furthermore, where known equivalents exist to specific features, such equivalents are incorporated as if specifically referred to in this specification.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in New Zealand or any other country.

Throughout this specification, and the claims which follow, unless the context requires otherwise, the words "comprise", "comprising" and the like, are to construed in an inclusive sense as opposed to an exclusive sense, that is to say, in the sense of "including, but not limited to".

CLAIMS

1. A starch product which contains up to approximately 10 % by weight lipid associated with starch in the starch product and where less than approximately 50 % by weight of the starch in the starch product has been gelatinised.
2. The starch product of claim 1 wherein it contains 0.5 to 2 % by weight lipid.
3. The starch product as claimed in claims 1 or 2 wherein less than approximately 10 % by weight of the starch in the starch product has been gelatinised, more preferably less than approximately 5 %.
4. The starch product as claimed in any one of claims 1 to 3 wherein the lipid may be any free fatty acid or any fatty acid derivative such as an ester of a fatty acid, or any combination or mixture thereof.
5. The starch product as claimed in claim 4 wherein the ester of a fatty acid is preferably a monoglyceride or a phospholipid.
6. The starch product as claimed in any one of claims 1 to 5 wherein the lipid present within the starch product is stabilised to decomposition.
7. The starch product as claimed in claim 6 wherein the lipid is stabilised to air oxidation.
8. A process for preparing the starch product of the first aspect of this invention including the steps:
    a) contacting an aqueous solution or emulsion of the lipid, or a salt of the lipid, with starch to form a mixture of the starch and the lipid; and
    b) where the ratio of water to starch in the mixture is above approximately 50 % by weight, heating the mixture to form the starch product at a temperature below the gelatinisation temperature of the starch; or
    c) where the ratio or water to starch in the mixture is below approximately 50 % by weight, heating the mixture to form the starch product at a temperature either above or below the gelatinisation temperature of the starch.
9. A starch product which contains one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives, where the starch product contains up to approximately 30% by weight of the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives in the starch product, and where the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives associate with the starch so that the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives are stabilised to decomposition.

10. A starch product as claimed in claim 9 wherein it contains up to approximately 10 % by weight of one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives.
11. A starch product as claimed in claim 9 or 10 wherein it contains less than approximately 5 % by weight of one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives.
12. A starch product as claimed in claims 9 or 10 wherein it contains less than approximately10 % by weight of a derivative of a polyunsaturated fatty acid.
13. A starch product as claimed in any one of claims 9 to 12 wherein the one or more polynsaturated fatty acid derivatives includes an ester of a polyunsaturated fatty acid.
14. A starch product as claimed in any one of claims 9 to 13 wherein the one or more polyunsaturated fatty acids includes an omega-3 fatty acid.
15. A starch product as claimed in claim 14 wherein the omega-3 fatty acid is one or more of α-linolenic acid, eicosapentaenoic acid (EPA) or docosahexaenoic acid (DHA).
16. A starch product as claimed in any one of claims 9 to 15 wherein the one or more polyunsaturated fatty acids and/or polyunsaturated fatty acid derivatives are stabilised to air oxidation.
17. A starch product which contains one or more omega-3 fatty acids or derivatives of omega-3 fatty acids, where the starch product contains up to approximately 10 % by weight of the one or more omega-3 fatty acids or derivatives thereof.
18. A process of making the starch products of any one of claims 9 to 17 the process comprising at least the steps of:
    a) contacting an aqueous solution or emulsion of the polyunsaturated fatty acid and/or polyunsaturated fatty acid derivative, with starch to form a mixture of the starch and the polyunsaturated fatty acid or derivative; and
    b) heating the mixture to a temperature above the gelatinisation temperature of the starch in the presence of water at greater than approximately 50% by weight of the starch.
19. A process as claimed in claim 18 wherein the heating of the mixture to a temperature above the gelatinisation temperature of the starch occurs in the presence of water at greater than approximately 100% by weight of the starch.
20. A process of making the starch products of any one of claims 9 to 17 the process comprising at least the steps of the method of claim 8.

21. A starch product as claimed in any one of claims 1 to 7 and 9 to17 wherein the starch is used in the form in which it occurs naturally.
22. A starch product as claimed in any one of claims 1 to 7, 9 to 17 and 21, wherein the starch product is either in its acidic or basic form.
23. The use of a starch product of any one of claims 1 to 7, 9 to 17, 21 and 22 in a food or as a food.
24. A food comprising at least a starch product of any one of claims 1 to 7, 9 to 17, 21 and 22.
25. A pharmaceutical comprising at least a starch product of any one of claims 1 to 7, 9 to 17, 21 and 22 optionally in association with one or more pharmaceutically acceptable carriers, diluents, and/or excipients.
26. The use of starch for the stabilisation of one or more lipids or salts thereof by adding the one or more unsaturated fatty acids and/or unsaturated fatty acid derivatives to starch.
27. The use of starch for the stabilisation of one or more polyunsaturated fatty acids or derivatives thereof by adding the one and/or more unsaturated fatty acids or unsaturated fatty acid derivatives to starch.
28. A starch product produced by a process of any of claims 8 or 18 to 20.
29. A process for making a food product comprising at least the step of preparing a starch product of any one of claims 1 to 7, 9 to 17, 21 and 22.
30. Use of a starch product of any one of claims 1 to 7, 9 to 17, 21 and 22 in the manufacture of a medicament for the prevention and/or amelioration of depression and/or coronary heart disease.
31. A starch-containing processed food in which starch is associated with one or more polyunsaturated fatty acids and/or their derivatives and wherein the one or more polyunsaturated fatty acids and/or their derivatives are stabilised to decomposition.
32. A starch-containing processed food in which starch is associated with one or more omega-3 fatty acids and/or their derivatives.
33. A process of making a starch-containing processed food the method comprising at least the step of adding one or more polyunsaturated fatty acids and/or their derivatives to one or more ingredients of the food during processing.
34. A starch-containing processed food obtained by a process as claimed in claim 32.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00114

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C08L 3/02; C08B 30/00, 30/12, 31/00; A21D 13/06; A23B 9/16, 9/24, 9/26; A23C 9/13, 9/137, 9/152, 9/154; A23D 7/06; A23L 1/0522, 1/10; C11B 5/00

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)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN FILE HCA, FSTA, WPIDS keywords: oleate, linoleate, oleic, linolenic, linolenate, linoleic, starch, anneal?, gelatinis?, gelatiniz?, stabilis?, stabiliz?, oxidat?, antioxidant, oxid?, amylose, lipid, fatty acid, surfactant, complex, unsaturated

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 2003/0044490 A1 (QI, H et al) 6 March 2003 See page 1 paragraphs 4, 5, 9, 16- page 2 paragraph 32, 36-40, 43, 46-47, page 3 paragraph 52, 59, 63, 65, 67-68, page 4 paragraph 69-71, page 5 paragraph 93, Table 5, claims 1-7.	1-7, 9-17, 21, 23-24, 26-27, 30-32
P,X	WO 02/074105 A1 (THONG SIEK FOOD INDUSTRY PTE LTD) 26 September 2002 See page 3 lines 15-32, page 4 lines 2, 17-20 and 30-32, page 5 lines 7-19, claims 1, 7-8	1-7, 9-17, 23-27, 29, 30-32

[X] Further documents are listed in the continuation of Box C

[X] 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 application or patent 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
4 September 2003	30 SEP 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **CHRISTINE BREMERS** Telephone No : (02) 6283 2313

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00114

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Number 2001-398990/43 B04, CN 1288735 (YU, LIN) 28 March 2001 See abstract	9, 14-17, 24-25
X	CA 2310986 A1 (SALIX CORPORATION,US et al) 17 May 2001 See example 1, claims 1, 6	1-7, 9-17, 23-24, 29, 31-32
X	US 5968896 A (BELL, S J et al) 19 October 1999 See column 2 lines 1-8, column 3 lines 34-41, claims 1, 22	1-7, 9-17, 24-25
X	WO 99/20111 A1 (THE PROCTER & GAMBLE COMPANY) 29 April 1999 See page 1 lines 12-13 and 19, page 2 lines 6-8 and 30 to page 3 line 5 and lines 18-19, page 4 lines 5-7, page 7 line 4-18, page 9 lines 15-17	1, 9, 2-24
X	Derwent Abstract Accession No. 99-193042/17 D13, FR 2768025 A1 (UNICOPA) 12 March 1999 See abstract	1-7, 24-25, 29
X	WO 98/21946 A1 (INTERNUTRIA, INC) 28 May 1998 See page 1 lines 5-17, page 6 line 17-page 7 line 6, page 12 lines 17-30, page 15 line 33-35, page 18 lines 16-33, page 19 lines 10-16	1, 21, 24-25, 29, 30
X	Derwent Abstract Accession No 98-289841/26 D13, JP 10099046 A (NIPPON OILS & FATS CO LTD) 21 April 1998 See abstract	1-7, 25-27, 291-7, 25-27, 29
X	AU 199724935 B2 (SOCIETE DES PRODUCTS NESTLE S.A.) 8 January 1998 See page 1a lines 4-5, 22-28, page 2 lines 4-8, 18-22, page 3 lines 11-16, page 4 lines 11-27, page 5 lines 8-10, example 1, claims 1-6, 13-18	1-20, 26-29, 31-34
X	Derwent Abstract Accession No 2001-092192/11 E17, CN 1145222 (GAOMING HIGH-TECH DEV CO LTD HARBIN) 19 March 1997 See abstract	1, 9, 14-17, 26, 27
X	US 5514212 A (KURRLE, F L) 7 May 1996 See column 2 lines 35-38, column 3 lines 45-55, table 1	26
X	Derwent Abstract Accession No 94-251659/31 D13, JP 06181725 (KITTY KK) 5 July 1994 See abstract	1-17, 26-27, 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00114

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5291877 A (CONDE-PETIT, B et al) 8 March 1994 See column 1 lines 9-48, column 2 lines 16-38, column 3 lines 24-34, column 4 lines 59-68 claim 1	1-5, 8, 21, 23-24, 29
X	EP 155915 B1 (HARDING, J A S) 23 November 1989 See page 2 lines 23-29, 49-54, page 3 line 50-52, page 4 lines 1-14	9-17, 21
X	WO 88/02221 A1 (KABIVITRUM AB) 7 April 1988 See page 1, lines 3-6, page 2 lines 1-19, page 3 lines 1-24, claims 1, 2, 8, 11-12	1-7, 9-17, 23-25, 29, 31-32
X	Derwent Abstract Accession No 88-050286/08 D13, DD 250048 A1 (AKADEMIE DER WISSENSCHAFTEN DER DDR) 30 September 1987 See abstract	1-7, 21, 23-24, 29
X	US 4562082 (MORIMOTO K) 31 December 1985 See abstract, column 1 lines 22-27, 63, column 2 lines 3-9, 29-30,67-68, column 3 lines 1-22, examples 1, 2, claim 1	1-7, 21, 23-24, 29
X	US 4491483 (DUDACEK, W E et al) 1 January 1985 See column 1 lines 26-30, column 2 lines 55-65, column 3 lines 15-30, 61- column 4 line 5, lines 40-55, page 6 lines 37-41, example 1A, example V parts A and B, claim 1	1-8, 21, 23-24, 28-29
X	Derwent Abstract Accession No 85-139587/23 A87 F01 L01, SU 1085946 A (SHEYANOVA A I) 15 April 1984 See abstract	1, 22
X	EP 0011479 B1 (GENERAL FOODS CORPORATION) 28 May 1980 See column 1 lines 37-43, column 2 lines 2-16,42-50, column 3 lines 9-46, column 4 lines 30-55, examples 1-VIII, claims	1-7, 21, 23-24, 29
X	GB 1505930 (KANSAS STATE UNIVERSITY RESEARCH FOUNDATION) 5 April 1978 See page 1 lines 15-23, page 2 lines 60-94, page 3 lines 77-86, page 4 lines 2-15, 45-65, page 7 lines 21-28, claim 1	1-7, 24, 29
X	GB 1493317 (SYNTEX (U.S.A.) INC 30 November 1977 See page 2 lines 20-38, page 3 lines 33-63, page 4 lines 6-11, 26-61, claims 1-13	1-7, 9-17, 23-25, 29, 31-32
X	US 3582350 (WERBIN, S et al) 1 June 1971 See column 1 line 59-column 2 line 12, lines 27-70, claim 1	1-8, 21, 23-24, 28-29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00114

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3537893 (HAUSER, N et al) 3 November 1970 See column 1 lines 34-38, column 2 lines 35-37, line 70-72, column 3 line 18, lines 32-45, column 4 lines 23-29, example I	1-8, 21, 28
X	US 3514298 (NOZNICK, P P et al) 26 May 1970 See abstract, column 1 line 68, column 2 lines 6-27, 54-59, column 3 lines 11-12, claims 1-5	1-5, 23-24
X	US 3443990 (DECNOP, C) 13 May 1969 See abstract, column 1 lines 68-72, column 2, column 3 lines 1-43, claims 1-2	1-8, 21, 23-24, 28-29
X	US 2827452 (SCHLENK, H et al) 18 March 1958 See column 1 lines 10-56, column 2 lines 8-72, column 3 lines 2-47, examples 8, 9, 12, 14, 15, claims 1, 11	1-7, 9-17, 21, 23-24, 26-27, 29, 31-32
X	GB 833458 (ROHM & HAAS COMPANY) 27 April 1960 See the example	1-4, 6-7, 24-25
X	YAMASHITA, M et al, "Effect of soy lysophospholipid on rheological properties of wheat starch gel", J. Appl. Glycosci., (2001) vol 48 no 3, pages 271-278 See abstract, page 271, page 273 column 2 lines 28-29, page 274 column 2 lines 4-8, 41-43	1-7, 21, 23-24, 29
X	STN FILE FSTA Abstract No 1999(06):M0623 & XIANGMIN, Z et al, Journal of the Chinese Cereals and Oils Association, (1988) vol 134 no 3, pages 16-20 See abstract	1-34
X	STN FILE HCA Abstract No 125:274177 & R. HOOVER et al, Food Chemistry (1996) vol 56 no 4, pages 355-367 See abstract	1-7, 9-17, 21, 24
X	STN FILE CA Abstract Number 88:87872 & JP 52127988 A2 (NIPPON KAYAKU CO., LTD.) 27 October 1977 See abstract	1-34
X	STN FILE FSTA Abstract No 1975(06):N0230 & G. BECKER et al, Fette, Seifen, Anstrichmittel, (1974) vol 76 no 10 pages 464-466	21, 24, 26-27
X	OHASHI, K et al "Effect of embraced lipid on the gelatinization of rice starch", Staerke (1980) vol 32 no 2 pages 54-58 See abstract , page 54 column 1, Tables 1, 2, page 57 "discussion"	1-7, 9-17, 21, 23-24, 26-27, 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00114

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STN FILE CA Abstract Number 31:43368 & LEHRMAN, L et al, Journal of the American Chemical Society (1937), vol 59 pages 1050-1051 See abstract	1-34
Y	CA 2034355 A1 (KSOLL, P et al) 19 July 1991 See page 3 lines 34-39, page 6 lines 7-18	1-7, 21, 23-24, 29
Y	US 3130118 (CHAPMAN, C H) 21 April 1964 See examples 1, 2	1-7, 21, 23-24, 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00114

Box I Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :

because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos : **1-34**

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The claims are broadly drafted such that a complete search was not economically feasible. Therefore the search was limited to the examples.

3. ☐ Claims Nos :

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/NZ03/00114

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
CA	2310986	NONE					
US	5968896	NONE					
AU	10984/99	WO	9920111	BR	9812958	CA	2306913
		EP	1024703				
WO	9821946	AU	52606/98				
AU	24935/97	BR	9703616	CA	2204421	CZ	9701864
		EP	813819	IL	120746	JP	10056984
		NZ	328096	PL	320586	SK	764/97
		US	5928707	ZA	9703993		
US	5514212	US	5411639				
US	5291877	AU	17109/92	BR	9202323	CA	2071265
		EP	519104	JP	6062770	NO	922344
		NZ	242942	PT	100608	ZA	9203771
EP	155915	IT	1199060	US	4606839		
WO	8802221	AU	80282/87	DK	2919/88	EP	266323
		EP	324762	FI	891478	NO	882311
US	4562082	CA	1220970				
US	4491483	AR	230149	AU	87276/82	BR	8205725
		DK	4344/82	EP	76381	ES	516097
		ES	8308929	FI	823172	GB	2107339
		JP	58076055	MY	331/86	NO	823303
		NZ	201592	PH	19049	PT	75587
		ZA	8206015	CA	1200422	PH	17651
GB	1505930	AU	84596/75	BE	833256	CA	1046336
		DE	2606826	DK	4678/75	ES	441617
		FR	2330329	IT	1056122	JP	51100479
		NL	7510902	SE	7509725		
GB	1493317	AT	3895/75	AU	79123/75	BE	829401
		CA	1062534	DE	2521815	ES	437911
		FI	751297	FR	2282902	JP	51026238
		NL	7506036	NO	751037	SE	7505717

		US	3950547				
US	3514298	NONE					
US	3443990	BE	669220	DE	1567354	NL	6410374
CA	2034355	AU	69404/91	DE	4001237	EP	437764
		FI	910252	JP	5038427	NO	910199
		US	5154763				
WO	02/074105	NONE					
WO	0011479	NONE					
US	3582350	NONE					
US	2827452	NONE					
GB	833458	NONE					
US	2003/0044490	WO	03/015528				
US	3582350	NONE					

END OF ANNEX