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(54) PROCESS FOR THE PRODUCTION OF SHORT CHAIN DIESTERS

VERFAHREN ZUR HERSTELLUNG VON KURZKETTIGEN DIESTER

PROCEDE D'ELABORATION DE DIESTERS A CHAINE COURTE

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Description

[0001] This invention is related to short chain diesters, and more particularly to a process for the obtain a product with a high content of zeaxanthin, lutein or mixtures thereof, as short chain organic acid diesters of zeaxantine, lutein or mixtures thereof.

B. DESCRIPTION OF THE RELATED ART.

[0002] The yellow carotenoids such as the lutein and the zeaxanthin, occur in marigold flowers as mono- or diesters , linked to long chain fatty acids such as palmitic, stearic or myristic acids, among others (Alam, A. U. (1968) *Lipids*, 3 (2), 183; Gayle G. (1986) *J. Food Sci.,* 51(4), 1093).

[0003] It is assumed that in such chemical structure, the carotenoids are better protected against oxidative processes, so that the flower color is better preserved in nature.

[0004] However, in the pigmentation of broilers, it has been shown that the bioavailability of such carotenoid fatty esters is lower than when they are hydrolized, i.e. when they are fed as free carotenoids (Coon, C.N. (1976) *Poult. Sci.*, 55, 841-847).

[0005] Applicant's have found that by saponification of the marigold carotenoids and their subsquent linking to short chain organic acids, such as formic, acetic propionic, etc., an improvement in their bioavailability, and that a more stable form of the carotenoids is achieved.

[0006] The acetylation of carotenoids, zeaxanthin among others, has been carried out in laboratory scale since decades ago. The reported methodology specifically refers to a research, for elucidation purposes about the chemical structures of the carotenoids.

[0007] The carotenoid in pure form, zeaxanthin in this case, is dissolved in pyridine treating it with acetic anhydride and agitation at room temperature to obtain the acetylated derivative after several hours (Liaaen-Jensen, S. and Jensen, A. (1971) *Methods Enzymol.* 23, 586), or in a few minutes if the reactants mixture is maintained under reflux (Alam, 1968).

[0008] Another preferred chemical path to obtain the acetylated compound is to dissolve the zeaxanthin in pyridine and benzene to carry on the reaction at 20° C with acetyl chloride, a few minutes later (Bartlett, L. (1969) *J. Chem. Soc.* C, 2538).

[0009] In the process according with the present invention, marigold extracts containing saponified and isomerized carotenoids (Torres, et al. 5,523,494 6/1996, 568/834), are treated directly with acetic anhydride, or propionic anhydride in such a way as to obtain the short chain organic acid diester derivatives of zeaxanthin, lutein or mixtures thereof, present in such extracts.

SUMMARY OF THE INVENTION

[0010] It is a main objective of the present invention to provide a product having a high content of zeaxanthin, lutein or mixtures thereof, in the form of short chain organic acid diesters of zeaxanthin, lutein or mixtures thereof, which can be used mainly in the pigmentation of broilers skin and egg yolks.

[0011] It is an additional main objective of the present invention to provide a process to obtain a product with a high content of zeaxanthin, lutein or mixtures thereof, in the form of short chain organic acid diesters of zeaxanthin, lutein or mixtures thereof, which can be used mainly in the pigmentation of broilers skin and egg yolks.

[0012] It is still a main objective of the present invention to provide a process of the above disclosed nature, by reacting short chain organic anhydrides to saponified extracts containing carotenoids, in an inert atmosphere of carbon dioxide, nitrogen or a mixture of both under controlled conditions of temperature and pressure.

[0013] It is another main objective of the present invention to provide a process of the above disclosed nature in which saponified extracts containing carotenoids are treated without the need to add of any solvent at all.

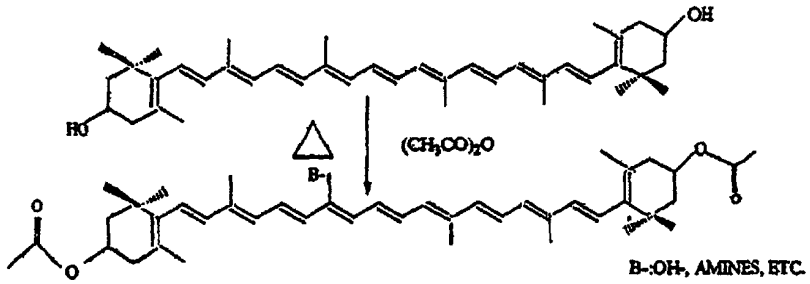
[0014] It is still another main objective of the present invention, to provide a process of the above disclosed nature, wherein the product or its formulations can be used for the pigmentation of broiler skin and egg yolk or as a pigmenting agent in aquaculture.

[0015] It is also an additional object of the present invention to provide a process of the above disclosed nature wherein the zeaxanthin diester obtained can be used as an intermediate in the synthesis of astaxanthin or cantaxanthin.

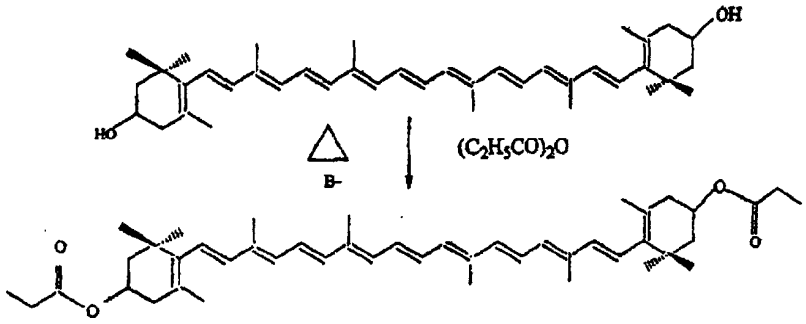
[0016] These and other objectives and advantages of the present invention will be apparent to those persons having ordinary skill in the art, from the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The chemical process is carried out according to the following reaction:



ZEAXANTHINE DIACETATE



ZEAXANTHINE DIPROPIONATE

[0018] The saponified marigold extract containing the zeaxanthin, has been obtained according to the procedure reported by Torres, et al. (1996), but any pigmenting formulation or extract containing zeaxanthin can be used. Regardless of the raw material employed, it should preferably be moisture free before acetylating with acetic anhydride, or before treatment with propionic anhydride.

[0019] The carotenoid containing substrate is maintained at a temperature in the range of 25°C to 140°C, but preferably between 40°C and 100°C.

[0020] When a crude marigold extract containing the saponified and isomerized carotenoids, enters into the reaction with the acetic or propionic anhydride, its residual fatty acids and other lipids present occur as the sodium or potassium salts.

Acetylation reaction

[0021] The acetic anhydride is slowly added to the extract in a reaction vessel under agitation, in a proportion from 0.2 to 2.0 parts by weight for one part of the pigmenting concentrate, which is in the form of a sodium or potassium soap (a heavy paste highly soluble in water). The reaction mixture is partially soluble in the acetic anhydride. However, as the acetylation reaction advances, an oily phase separates from the reaction media, mainly composed of acetic acid and sodium or potassium acetates in aqueous solution, from which it easily separated by decanting. The acetylation vessel wherein the reaction takes place should be kept under an inert atmosphere, in order to avoid the intensive degradation of the xanthophylls. An inert diluent such as ethylene glycol or propylene glycol or an aliphatic or cyclic hydrocarbon can be used to reduce the viscosity of the mixture.

[0022] The reaction time depends on the temperature and can be from 6 minutes to 24 hours, but preferably from 4 to 18 hours.

Parameter	Trial 1	Trial 2	Trial 3	Trial 4
Acetic anhydride: extract Ratio	0.5	2.5	1.0	2.0
Reaction time, hrs.	16	16	20	12
Reaction temperature, °C	90	80	100	60
Pressure, mm Hg	750	760	750	760
Mono-hydroxycarotenoids %	4.2	1.5	1.7	2.8
Di-hydroxycarotenoids %	2.1	1.3	1.3	0.8

(continued)

Parameter	Trial 1	Trial 2	Trial 3	Trial 4
Aceto-carotenoids %	88.5	91.8	89.6	90.2

Propionation reaction

[0023] Propionic anhydride is slowly added to the extract in a reaction vessel under agitation, in a proportion from 0.2 to 3.0 parts by weight to one part of the pigmenting concentrate, which is in the form of sodium or potassium soap (a heavy paste highly soluble in water). The reaction mix is partially soluble in the propionic anhydride. However as the propionation reaction advances, an oily phase separates from the reaction media, mainly composed of propionic acid and sodium or potassium propionates in aqueous solution, from which it is easily separated by decanting. The reaction vessel should be kept under an inert atmosphere to avoid degradation.

[0024] The reaction time depends on the temperature and can be from 5 minutes to 24 hours, but preferably from 3 to 17 hours.

Parameter	Trial 1	Trial 2	Trial 3	Trial 4
Propionic Anhydride:extract Ratio	0.8	2.5	2.0	3.0
Reaction time, hrs.	6	4	4	3
Reaction temperature, °C	70	60	80	80
Pressure, mm Hg.	760	780	760	780
Mono-hydroxycarotenoids %	4.1	1.5	1.8	0.7
Di-hydroxycarotenoids %	2.3	1.0	0.6	1.0
Propionate-carotenoids	86.0	90.0	89.0	91.0

[0025] The saponified extracts used as the raw material in the above described process, contain approximately 92 % of di-hydroxy carotenoids, and 1-2% of mono-hydroxy carotenoids, quantified according to the AOAC method.

[0026] The identification and quantification of the pigments involved were carried out following the HPLC techniques mentioned by Torres, et al.(1996), as well as by the use of other spectroscopic techniques as IR, UV, ^{1}HNMR, etc., widely used in carotenoids identification.

[0027] The end product can be formulated as an aqueous emulsion, or it can be dispersed by means of a carrier to obtain pre-mixtures of a given concentration of zeaxanthin, lutein or mixtures thereof in the form of short chain organic acid diesters, to be used as a pigmenting agent for broiler's skin, egg yolks, or shrimps and salmon in aquaculture.

Claims

1. A process for obtaining organic acid diesters of mono- or polyhydroxilated carotenoids from saponified extracts containing carotenoids, comprising: reacting 0.2 to 2.0 parts by weight of acetic anhydride or 0.2 to 3.5 parts by weight of propionic anhydride, slowly under agitation, each with one part of said saponified extracts containing carotenoids, saponified with sodium or potassium hydroxide, in the absence of solvents.

2. The process as claimed in claim 1, wherein the carotenoids are selected from lutein and zeaxanthin.

3. The process as claimed in claim 1, wherein saponified extracts containing carotenoids are obtained from extracts of marigold flowers, marigold meal, yellow corn, yellow corn gluten, or alfalfa.

4. The process as claimed in claim 1, wherein the saponified extract is moisture free.

5. The process as claimed in claim 1, wherein the saponified extract contains residual NaOH or KOH.

6. The process as claimed in claim 1, wherein the reaction time is from 5 minutes to 12 hours, preferably from 2 to 10 hours.

7. The process as claimed in claim 1, wherein the reaction temperature is from 25 to 140°C, preferably from 40 to 100°C.

8. The process as claimed in claim 1, wherein the reaction is carried out in an inert atmosphere of carbon dioxide, nitrogen, or a mixture of both.

9. The process as claimed in claim 1, wherein the proportion of acetic anhydride is from 0.5 to 1.5 parts by weight for one part of extract, or wherein the proportion of propionic anhydride is from 0.5 to 1.5 parts by weight for one part of extract.

Patentansprüche

1. Verfahren zur Herstellung von Diestern von monooder polyhydroxylierten Carotinoiden aus verseiften Carotinoid-haltigen Extrakten mit organischen Säuren, bei dem man 0,2 bis 2,0 Gewichtsteile Essigsäureanhydrid bzw. 0,2 bis 3,5 Gewichtsteile Propionsäureanhydrid langsam unter Rühren jeweils mit einem Teil der mit Natrium- oder Kaliumhydroxid verseiften Carotinoid-haltigen Extrakte ohne Lösungsmittel umsetzt.

2. Verfahren nach Anspruch 1, bei dem man die Carotinoide unter Lutein und Zeaxanthin auswählt.

3. Verfahren nach Anspruch 1, bei dem die verseiften Carotinoid-haltigen Extrakte aus Extrakten von Ringelblumenblüten, Ringelblumenmehl, Gelbmais, Gelbmaisgluten oder Alfalfa erhalten werden.

4. Verfahren nach Anspruch 1, bei dem das verseifte Extrakt feuchtigkeitsfrei ist.

5. Verfahren nach Anspruch 1, bei dem das verseifte Extrakt NaOH- bzw. KOH-Reste enthält.

6. Verfahren nach Anspruch 1, bei dem die Reaktionszeit 5 Minuten bis 12 Stunden, vorzugsweise 2 bis 10 Stunden, beträgt.

7. Verfahren nach Anspruch 1, bei dem die Reaktionstemperatur 25 bis 140°C, vorzugsweise 40 bis 100°C, beträgt.

8. Verfahren nach Anspruch 1, bei dem man die Umsetzung in einer Inertatmosphäre aus Kohlendioxid, Stickstoff oder einem Gemisch davon durchführt.

9. Verfahren nach Anspruch 1, bei dem der Essigsäureanhydrid-Anteil 0,5 bis 1,5 Gewichtsteile pro Teil Extrakt bzw. der Propionsäureanhydrid-Anteil 0,5 bis 1,5 Gewichtsteile pro Teil Extrakt beträgt.

Revendications

1. Un procédé d'obtention de diesters acides organiques de caroténoïdes mono- et polyhydroxylés à partir d'extraits saponifiés contenant des caroténoïdes, comprenant : la réaction de 0,2 à 2,0 parties en poids d'anhydride acétique ou 0,2 à 3,5 parties en poids d'anhydride propionique, lentement sous agitation, dans chaque cas avec une partie desdits extraits saponifiés contenant des caroténoïdes, saponifiés avec de l'hydroxyde de sodium ou de potassium, en l'absence de solvants.

2. Le procédé de la revendication 1, où les caroténoïdes sont choisis parmi la lutéine et la zéaxanthine.

3. Le procédé de la revendication 1, où les extraits saponifiés contenant des caroténoïdes sont obtenus à partir d'extraits de fleurs de souci, de farine de souci, de maïs jaune, de gluten de maïs jaune ou de luzerne.

4. Le procédé de la revendication 1, où l'extrait saponifié est dépourvu d'humidité.

5. Le procédé de la revendication 1, où l'extrait saponifié contient des résidus de NaOH ou KOH.

6. Le procédé de la revendication 1, où le temps de réaction est compris entre 5 minutes et 12 heures, de préférence entre 2 et 10 heures.

7. Le procédé de la revendication 1, où la température de réaction est comprise entre 25 et 140 °C, de préférence entre 40 et 100 °C.

8. Le procédé de la revendication 1, où la réaction a lieu dans une atmosphère inerte de dioxyde de carbone, d'azote ou d'un mélange de deux.

9. Le procédé de la revendication 1, où la proportion d'anhydride acétique est comprise entre 0,5 et 1,5 parties en poids pour une partie d'extrait, ou bien la proportion d'anhydride propionique est comprise entre 0,5 et 1,5 parties en poids pour une partie d'extrait.