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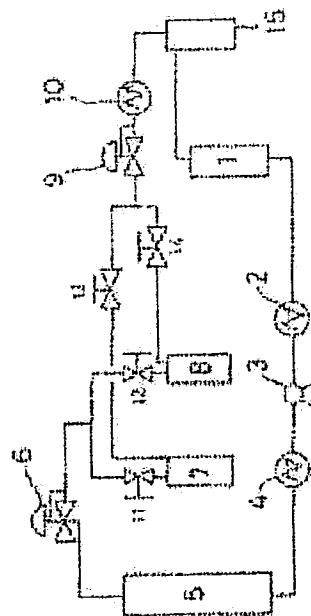
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METHOD FOR EXTRACTING AND SEPARATING COLORING MATTER FROM KRILL

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Abstract of JP4057853 (A)

PURPOSE: To prepare a reddish orange coloring matter having a high safety in a high concn. by extracting, with CO₂ in a supercritical state, krill shells of which the protein has been decomposed by a protease. CONSTITUTION: Krill shells are treated with a protease to decompose the protein in the shells and the treatment product is filtered. The residue of filtration is dried to give treated shells having a water content of 6-8% and a mean particle size of 200 μm or lower. The treated shells are put into an extraction vessel 5. An extractant comprising a liq.; CO₂ in an amt. of 30-40 pts.wt. based on one pt.wt. treated shells having a coloring matter concn. of 30 mg/100 g is supplied through a supercooling apparatus 2 to a pump 3, pressurized at the pump 3 to 100-250 kg/cm², heated with a heat exchanger 4 to 35-40 deg.C to bring it into a supercritical state, and transferred to the extraction vessel 5 to extract an oil in the treated shells. After the pressure of the oil-contg.



CO₂ in the supercritical state is reduced to 40-60 kg/cm² with a pressure reducing valve 6, the CO₂ is delivered through a selector valve 11 to the first separating vessel 7 to separate the oil, and recycled through a selector valve 13, a pressure reducing valve 9, a condense 10, a water separator 15, and a storage vessel 1 to the extraction vessel 5.; Then, selector valves 11 and 13 are closed while selector valves 12 and 14 are opened, and the CO₂ contg. the coloring matter is transferred to the second separating

vessels, where the CO₂ is evaporated to give a coloring matter with a concn. of 2000-10000 mg/100g.

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(54) Title of Invention: METHOD FOR EXTRACTING AND SEPARATING PIGMENT FROM KRILL

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Specification

1. Title of Invention

Method for extracting and separating pigment from krill

2. Claims

(1) A method for extracting and separating pigment from krill, wherein, using as a starting material krill shells that are the residue after krill has been decomposed by a protease and the protein removed, pigment is extracted and separated with supercritical carbon dioxide as an extraction agent.

(2) The method for extracting and separating pigment from krill according to claim 1, wherein extraction and separation are characterized in that

the extract from the krill shells is fractionated while varying the pressure of supercritical carbon dioxide in two stages.

(3) The method for extracting and separating pigment from krill according to claim 1, wherein extraction and separation are characterized in that the extract from the krill shells is fractionated by separation over time without varying the pressure of supercritical carbon dioxide.

(4) The method for extracting and separating pigment from krill according to claim 1, wherein extraction and separation are characterized in that components extracted in an extraction tank are fractionated by a plurality of separation tanks of different conditions.

(5) The method for extracting and separating pigment from krill according to any one of claims 1 through 4, characterized in that the moisture content ratio of krill shells is from 10% to 30%.

3. Detailed Description of the Invention (Industrial Field of Use)

The present invention relates to a method for obtaining high-concentration pigment by separating the reddish-orange pigment having a primary component of astaxanthin contained in krill, and in particular, it relates to a method of extraction and separation using supercritical carbon dioxide.

(Prior Art)

The reddish-orange pigment having a primary component of astaxanthin contained in krill has generally been extracted from krill organisms using an organic solvent. This extract contains various components, starting with the lipids that are contained in krill. In particular, concentration and separation of only the pigment contained in the pigment extract is necessary because oxidative decomposition products such as unsaturated fatty acids and glycerol esters thereof bonded to or coexisting with the pigment give off an unpleasant odor, or reaction products in the course of oxidative decomposition such as unsaturated fatty acids cause fading of the pigment.

As methods for concentrating and separating pigment from krill pigment extract liquid, Japanese Unexamined Patent Application Publication No. S60-4558 and Japanese Examined Patent Application Publication No. S61-52183 propose a method in which the pH of krill pigment extract liquid extracted by an organic solvent such as n-hexane or acetone is neutralized and lipids are then decomposed by a lipase, and a method in which pigment liquid is separated from a liquid in which an alkali has been added to decompose lipids or other impurities, and then this pigment liquid is extracted and separated by molecular distillation or by a fluid in the supercritical state.

(Problems the Invention is to Solve)

In the proposed krill pigment concentration and separation methods of prior art, numerous steps are required, including a step of extracting krill pigment liquid from krill organisms by an organic solvent, a neutralization step, a step of decomposing lipids and impurities by lipase or alkali, a step of decomposing the decomposition products of impurities and krill

pigment, and an extraction step by molecular distillation or a fluid in the supercritical state.

Furthermore, it has been reported that the reddish-orange pigment contained in krill has astaxanthin as a primary component and has 100 to 1000 times the antioxidant action of vitamin E, and is anticipated to be used as a drug starting substance in the future. If used as a drug starting substance, however, steps such as solvent removal will be required in order to completely eliminate residue of the organic solvent used in the krill pigment liquid extraction step.

A method has also been considered wherein krill are extracted directly by supercritical carbon dioxide without going through treatment steps, but it is difficult to extract and separate only the pigment because the large amount of moisture and various useful components contained in krill are simultaneously extracted.

(Means for Solving Problems)

The present inventors arrived at the present invention as a result of diligent research to solve the above problems.

Since krill contains a large amount of useful components such as proteins, it has been used in applications such as starting materials for processed foods. Among these applications, the proteins contained in krill have been separated and used in the starting materials of amino acids, rather than krill being used as is. However, the krill shells from which such proteins used in starting materials of amino acids have been removed were discarded or only used as feed for cultivated fish in the past.

The present inventors discovered that krill pigment is produced without going through special pretreatment steps by employing a simple method wherein krill pigment liquid is extracted from krill using a supercritical fluid, by using the shells remaining after components such as proteins from krill have been removed as the starting material of pigment production.

That is to say, pigment is extracted by a supercritical fluid using as a starting material krill shells that are the residue obtained by methods such as filtration after the useful components such as proteins in the krill have been decomposed by enzymes.

The supercritical fluid in the present invention is a fluid in a state beyond the critical temperature and critical pressure. In the case of carbon dioxide, it is the state at 31°C or above, 75.3 Kg/cm² or above;

for propane, 96.7°C or above, 43.4 Kg/cm² or above; for ethane, 9.9°C or above, 52.2 Kg/cm² or above. These fluids are characterized by having density close to that of a liquid and a large expansion coefficient close to that of a gas, and can be used in extraction and separation of various organic matter. In the method of the present invention, carbon dioxide in particular is used as the supercritical fluid. When carbon dioxide gas is used, not only are the steps required in extraction and separation of pigment simplified, but there is absolutely no danger even if the carbon dioxide used as the extraction agent remains in the extracted pigment, for example, and the obtained pigment can be used without a problem in many fields starting with pharmaceuticals.

Additionally, supercritical carbon dioxide used as an extraction agent has no risk of explosion or combustion in air like hydrocarbons do. Furthermore, since the critical temperature and critical pressure of carbon dioxide are relatively low, dissolution characteristics can be easily varied by varying the temperature and pressure, and it is possible to perform extraction with an extraction agent having dissolution characteristics suited to pigment extraction and separation.

The method of the present invention is to extract pigment with supercritical carbon dioxide using krill shells as a starting material. The method of the present invention was achieved by studying the extraction conditions such as extraction pressure, temperature and fractionation method for performing efficient extraction and separation of pigment, and by studying the water content ratio of the starting material krill.

The present invention will be described below in reference to the drawings.

FIG. 1 is a flowchart of equipment having a means for switching among a plurality of separation tanks for implementing the method of the present invention.

The extraction agent carbon dioxide passes from a liquid carbon dioxide storage tank 1 to a supercooler 2, after which it is pressurized to a prescribed pressure by a pump 3, and then heated to a prescribed temperature by a heat exchanger 4, and supplied as supercritical carbon dioxide to an extraction tank 5 filled with krill shells.

The starting material krill shells primarily contain chitin, proteins, triglyceride esters, triglyceride

esters, monoglyceride esters (oil components) and pigment (astaxanthin). The residue obtained when frozen krill is thawed and then the extract portion in which the proteins decomposed by a protease have been filtered out is a powder with an average particle size of 200 μm, and normally has a water content ratio of 6% to 8% after it is dried.

Since supercritical carbon dioxide has the characteristic that it decomposes the oil components and pigment of krill shells, only two components are extracted from the krill shells, but in order to separate these two components, the extraction operation is divided into two stages.

Namely, in the first extraction, the oil components contained in the krill shells are extracted by passing through 30 parts by weight to 40 parts by weight of supercritical carbon dioxide having a temperature of 30°C to 50°C and a relatively low pressure of 100 Kg/cm² to 250 Kg/cm² for every 1 part by weight of krill shells having a pigment concentration of 30 mg/100 g, which is equivalent to the concentration of contained astaxanthin.

The supercritical carbon dioxide that contains oil components is reduced in pressure to 40 Kg/cm² to 60 Kg/cm² by a pressure reducing valve 6, and led into a first separation tank 7 via a switching valve 11.

In the first separation tank 7, carbon dioxide in the gas state which has separated the oil components is further reduced in pressure and adiabatically expanded by a switching valve 13 and a pressure reducing valve 9, and after being liquefied by a condenser 10, it passes through a water separator 15 and returns to the liquid carbon dioxide storage tank 1 where it is recirculated.

Then, supercritical carbon dioxide is supplied to the extraction tank 5 at a pressure higher than the pressure during the first extraction stage. That is, 30 parts by weight to 40 parts by weight of supercritical carbon dioxide having a temperature of 30°C to 50°C and a pressure of 300 Kg/cm² to 500 Kg/cm² is supplied to the extraction tank for every 1 part by weight of krill shells, and by closing the switching valves 11 and 13 and opening switching valves 12 and 14, carbon dioxide containing extract with a pressure of 40 Kg/cm² to 60 Kg/cm² is led to a second separation tank 8 by the pressure reducing valve 6.

In the second separation tank 8, carbon dioxide in the gas state is returned to the liquid carbon dioxide

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