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(54) **Title**: METHOD FOR TREATING BIRCH BARK AND THE USE OF THE PRODUCT

(57) **Abstract**: The present invention provides an improved method for obtaining a bark extract by hydrolysis and acidification in the presence of water. The method comprises the steps of subjecting birch bark to hydrolysis; separating the undissolved bark portions from the hydrolysis liquid; providing a liquid phase and acidifying this liquid phase; precipitating the extracts from the liquid phase by raising the relative amount of water in the liquid phase and recovering the extract. Further the invention relates to an animal feed obtainable by this method and to the use of the birch bark extract in food, animal feed, pulp, paper and board, pigments and barriers for paper coating.

Method for treating birch bark and the use of the product

FIELD OF THE INVENTION

The present invention relates to a method for recovering a birch bark extract comprising the steps of subjecting birch bark to hydrolysis using a hydrolysis liquid comprising solvent, separating the undissolved bark portions from solvent liquid remaining after the hydrolysis; providing a liquid phase comprising said solvent liquid, acidifying the liquid phase; precipitating the extracts from the liquid phase by raising the relative amount of water in the liquid phase; recovering the extract. Further the invention relates to an animal feed obtainable by this method and to the use of the birch bark extract in food, animal feed, pulp, paper and board, pigments and barriers for paper coating.

BACKGROUND OF THE INVENTION

Birch bark is a potential source of a variety of organic chemicals and the chemical substances of birch bark has shown to be effective in different pharmaceutical and industrial applications. Birch outer bark contains for example betulinol, suberin and phenolic groups, in general birch bark comprises 30 to 60 % of suberin consisting of long chain fatty acids. Part of the fatty acids contains epoxy groups and other functionalities, such as hydroxyl groups. The fatty acids can also be bond to phenolic groups. Different *Betula* species has been described to be remarkable suberin sources.

Different methods for isolation of birch bark extracts have been described in WO 2007/045728 A1 and US 4,732,708 where an oxidation step is carried out at 200-400 °C with potassium permanganate or chromic acid and in WO 2007/121482 A1 where pure betulinol and suberin fatty acids are isolated involving purification of the extract with water insoluble solvents and crystallization of betulinol from this solvent fraction. In US 7,264,184 a sequential isolation method for pure suberin acids is described, in US 7,198,808 a method for extracting betulin and lupeol is described and WO 2008/027426 A1 relates to pelletizing birch bark with alkali prior to extraction for pure betulinol production. WO 2010/093320 describes a method for separating a suberin monomer from a suberin and/or cutin containing plant material. The previous described methods all describe isolation and purification of certain birch bark components.

It should be noted that all documents cited in this text ("herein cited documents") as well as each document or reference cited in each of the herein-cited documents, and all manufacturer's literature, specifications, instructions, product data sheets, material data sheets, and the like, as to the products and processes mentioned in this text, are hereby expressly incorporated herein by reference.

SUMMARY OF THE INVENTION

The present invention relates to a method for treating birch bark in order to recover birch bark extract. The method comprises subjecting birch bark to hydrolysis; separating the undissolved bark portions from the liquid phase; acidifying the liquid phase; precipitating the extracts from the liquid phase by raising the relative amount of water in the liquid phase; separating and/or recovering the extract. Further the invention relates to an animal feed obtainable by this method and to the use of the birch bark extract in food, animal feed, pulp, paper and board, pigments, barriers for paper coating etc.

One advantage of the invention on hand is that modifying the water content after hydrolysis and acidification increases the yield and quality of the extract product and improves the stability of the process. The raised water content is achieved by adding surplus water after the acidification and/or for example by evaporating the solvent from the acidified hydrolysis liquid.

A still further advantage of the invention is that the water content during the precipitation also takes part in the removal of salts formed during the acidification of the alkaline hydrolysis liquid. This solves the prior art problem where the formed salt remains in the final product. The quality of the product is improved since the washing removes impurities from the extract.

Moreover, a further advantage of the invention is that the birch bark extraction process is more stable if the hydrolysis is performed with a controlled concentration of water in the solvent. A preferred embodiment of the invention solves the problem of prolonged hydrolysis as the hydrolysis solution does not have to contain excess water. The birch bark extraction methods previously known in the art have been unstable due to problems in controlling hydrolysis. Especially if more water is present in the hydrolysis solution, this leads to a too invasive hydrolysis, where the suberin lignin structure is also broken down.

This causes excess aromatic impurities in the final product and thereto the removal of the hydrolysis liquid and precipitation is difficult as the birch bark softens.

An additional advantage of the bark extracts of the invention is that they are natural products which have a sustainable and environmentally friendly character. They have a generally low toxicity and are well tolerated at levels which are effective in affecting for example animal digestive tract microbiota.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of one method of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an improved method for obtaining a bark extract by hydrolysis and acidification in the presence of water.

In the present specification and claims, the following terms have the meanings defined below.

The term "extract" as used in the description and claims refers to the product received by the method of the invention. Preferably the extract comprises and/or contains suberin fatty acids, betulinol, phenolic complexes and/or combinations thereof. In order to receive an extract with a higher amount of dry matter the extract is optionally concentrated. A higher amount of water during precipitation typically leads to a higher amount of betulinol in the extract and a lower amount of water respectively to a higher amount of fatty acids.

The term "hydrolysis liquid" refers to the liquid used for hydrolysis. Preferably the liquid used for alkaline hydrolysis of for example processed birch bark comprises or consists of alkali hydroxide, solvent and water wherein the amount of water is 5 to 50 w-%, preferably 10 to 30 w-%, more preferably 15 to 25 w-%, most preferably about 20 w-% of the total amount of liquids.

The term "bark" refers to birch bark from different Betula species containing mainly outer birch bark.

The term "solvent" refers to different solvents typically used in the present invention for hydrolysis and/or washing. These solvents comprise; alcohols, such as ethanol or isopropanol; acetone; cyclohexane; ethyl acetate; water; or mixtures thereof.

The term "feed" or "animal feed" as used in the description and claims refers to the total feed composition of an animal diet or to a part of it. Thus, unless specifically stated, the term "feed" or "animal feed" should be taken to mean to include supplemental feed, premixes, water or other liquids for drinking etc. The feed may comprise different active ingredients.

The term "animal" as used in the description and claims refers to all kind of different animals, such as monogastric animals, ruminants and aquaculture including fish and shellfish. The animals may be production animals as well as pets. Examples of different animals, including offspring, comprise cows, beef cattle, pigs, poultry, sheep, goats, horses, cats, dogs, shrimps and scampi.

The present invention relates to a method for recovering from birch bark a product extract comprising the following steps or any preferred combinations thereof:

a) Mechanically processing birch bark, preferably by log peeling, chipping, crushing, grinding, shredding, milling or by any combinations thereof. The inner and outer bark is typically separated by for example screening or with water separation. In water separation the outer bark is typically floating and the inner bark is getting wet and sinking.

b) Subjecting birch bark to hydrolysis using a hydrolysis liquid comprising solvent preferably alkaline hydrolysis using a hydrolysis liquid comprising solvent alkali hydroxide, solvent and water wherein the amount of water in the hydrolysis liquid typically is 5 to 50 % of the total amount of liquids, preferably 10 to 30 w-%, more preferably 15 to 25 w-%, most preferably about 20 w-%. Preferably the solvent added in step b) is added at almost boiling temperature.

c) Separating the undissolved bark portions from the solvent liquid remaining after hydrolysis. Typically the undissolved bark portion is further washed with solvent and/or steamed in order to remove solvent from it. In a preferred embodiment of the invention the solvent and/or steam mixture is typically combined with the solvent liquid to form a liquid phase.

d) Acidifying the liquid phase, wherein the pH is adjusted to a pH from pH 4 to pH 2, more preferably from pH 3 to pH 2, including pH being from pH 3,9, 3,8, 3,7, 3,6, 3,5, 3,4, 3,3, 3,2, 3,1, 2,9, 2,8, 2,7, 2,6, 2,5, 2,4, 2,3, 2,2 or 2,1 to pH 2. In a preferred embodiment hydrochloric acid is used for acidifying.

e) Precipitating the extracts from the liquid phase by raising the relative amount of water in the liquid phase. The preferred amount of water during the precipitating stage is between 30 and 70 v-%, more preferably 55 and 65 v-%, most preferably about 60 v-% of water of the total amount of liquids, including the preferred amount of water being from 68, 63, 60, 58, 53, 50, 48, 45, 43, 40, 38, 35, 33 v-% to 30 v-%. In preferred embodiments of the invention the relative amount of the water content is raised by adding surplus water to the liquid phase and/or by evaporating the solvent from the acidified liquid phase, typically by adding 30 and 70 v-%, more preferably 45 and 55 v-%, most preferably about the same volume of water to the liquid phase.

f) Separating and/or recovering the extract. Typically the precipitated and washed extract of step e) is filtered and optionally concentrated by evaporation preferably at a temperature from 70 to 90 °C, more preferably from 70 to 80 °C before drying. In preferred embodiments of the invention the drying is performed in a batch-type vacuum dryer, for example a horizontal Lödige Druvatherm, in a spray-dryer or in a thin-film evaporator. Typically a carrier is added to the extract before drying. In a preferred embodiment of the invention the carrier is diatomaceous earth, preferably added in an amount of 1 to 60 w-%, more preferably 30 to 50 w-%, most preferably about 40 w-% of the total dry matter. An advantage of adding diatomaceous earth to the extract as carrier before drying is that it decreases the stickiness of the extract and thereto neutralizes the extract. It is also possible to dry the product without adding a carrier.

In preferred embodiments of the invention the birch bark extract comprises a combination of compounds or components of birch bark (*Betula*). Typically the raw material used for

the birch bark extract is bark of *Betula pubenscens, Betula verrucosa (Betula pendula)* and/or *Betula papyrifera*.

The solvent used for hydrolysis and/or washing is typically alcohol; acetone; cyclohexane; ethyl acetate; water or mixtures thereof. Preferably the solvent used for hydrolysis is alcohol, most preferably ethanol or isopropanol. In a preferred embodiment of the invention water is used for washing the precipitated extract of the invention. This water used for filtration and/or washing removes extra salts and other impurities from the extract.

The invention further relates to an animal feed obtainable by the method of the invention described above. In preferred embodiments of the invention the animal feed is part of the feed preferably a supplemental feed, premix or liquid for drinking.

The animal feed of the invention is typically given to animals such as monogastric animals, ruminants and aquaculture, preferably cows, beef cattle, pigs, poultry, sheep, goats, horses, cats, dogs, fish and shellfish.

Another aspect of the invention is the use of the birch bark extract obtained or produced by the method of the invention described above in food, animal feed, pulp, paper and board, pigments and barriers for paper coating.

A preferred embodiment for preparation of a birch bark extract according to the method of the invention starts with raw material pre-treatment comprising one or more of mechanical log peeling, mechanical chipping/crushing, water separation, drying to a residual humidity below 23 %, preferably below 20 %, most preferably below 15 % and eventually intermediate storage.

In a preferred process of the invention the solvent is added at almost boiling temperature after charging the reactor with birch bark. Although the solid-liquid extraction is preferably performed at atmospheric pressure it is also possible to use pressure. During the extraction the mixture is typically kept at boiling temperature. The extracts are transferred from the raw material to the solvent and the concentration of the extractives is typically from 2 to 5 w-%. The solvent containing the extracts, i.e. the liquid from the hydrolysis is

thereafter removed from the bark residue and the solvent liquid is filtered and stored in the process tank. The bark residue is washed, preferably with pure solvent, most preferably with 80 w-% IPA. After washing, the washing solvent is typically also stored in the process tank. The bark is preferably steamed in a reactor or washed with for example water to get the rest of the solvent out of the bark where after the evaporated solvent and/or the steam mixture is optionally distilled. The solvent with which the undissolved bark residue is washed is optionally combined with the solvent liquid to provide a liquid phase which is treated further. The steam mixture is also optionally combined with the solvent liquid and/or washing solvent to provide the liquid phase.

In the method according to the invention the used bark residues are for example used in energy production. The bark residues are either dried or used as such.

In this preferred embodiment of the invention the liquid phase comprising the extracts is there after adjusted from alkali to acidic, preferably to a pH from pH 4 to pH 2, more preferably from pH 3 to pH 2 with an acid such as hydrochloric acid (HCl) or sulphuric acid (H_2SO_4). Although any other acid can be used, hydrochloric acid is preferred since the use of other acids may affect the taste of the feed. Another aspect is that the sodium chloride is relatively easy to wash compared to other salts. However, depending on the use of the birch bark extract of the invention also other acids may be used. Preferably the extracts precipitate after acidification of the liquid phase and water addition and the mixture is then pumped to a filter for separation of the precipitated dry matter. Typically some water is pumped to the filter in order to wash and remove extra salts and other impurities of the extract.

After precipitation the concentration of the extract is typically approximately 20 w-% why this slurry is preferably fed into an intermediate evaporation tank and concentrated to an approximately 60 w-% extract. The evaporation can be performed at atmospheric pressure or by vacuum and the temperature is preferably from 70 to 90 °C, more preferably from 70 to 80 °C. The concentrated liquid is there after ready to be sent to a final dryer and the evaporated gas is advantageously distilled.

The final drying is performed by conventional drying techniques; preferably the dryer is a batch-type vacuum dryer, most preferably a horizontal Lödige Druvatherm or a spray-

dryer. A thin-film evaporator or rising film evaporator can also be used for the drying. Typically a carrier, preferably diatomaceous earth, is added by constant mixing before drying and the drying conditions are about 40 kPa (a) and from 70 to 80 °C.

According to a preferred embodiment of the invention the solvents and the water is reused and/or the solvent is circulated for example through a distilling colon.

In preferred embodiments of the invention multiple reactors are used in sequences so that the reactors are in different batch phases.

Fig 1 shows a schematic flow diagram of one preferred method of the invention, where the feed 1 is fed to a reactor for hydrolysis 2, where after the extraction liquid is separated from the solid material with washing 3 and precipitation is performed by adjusting the pH and water concentration 4. The precipitated material is separated 5 and the solvent is evaporated and the extract is concentrated and/or dried 6. The product is stored 7 and the solvent or water mixture is distilled 8 and stored 9 in solvent storage tanks.

In the present specification and claims, the percentages or amounts of the components of the extracts and/or feed are calculated on the dry solids content by weight unless otherwise specified.

The following examples are given to further illustrate the invention and are not intended to limit the scope thereof. Based on the above description a person skilled in the art will be able to modify the invention in many ways to provide birch bark extracts according to the method of the invention.

Comparative example 1 according to US 2009/0182158 A1, Ex. 1

Outer birch bark (15 g) was added to a 0,5 N solution of NaOH (3.5 g in 2 ml of water) and Isopropyl alcohol (IPA, 150 ml) at 50°C. The reaction mixture was cooked for 3 hrs and then filtered. The solid portion recovered from the filter was refluxed with IPA (100 ml) for 0.5 hr and again filtered. The procedure was repeated a third time with 100 ml of IPA. The isopropanol extracts were combined and the solvent was evaporated yielding a solid residue.

The solid residue was desiccated, 100 ml heptane was added. Heptane was used instead of xylene since xylene is aromatic, carcinogenic and toxic and is hard to use in full scale. Suspending the dry solid residue to the heptane was challenging due to its stacking character and high viscosity. The mixture was cooked for 1 hr and then filtered at about 100°C. The solid residue recovered from the filter was cooked again. The heptane phases where combined and evaporated. The yield of betulinol was 6,5%. The solid residue from the filter was treated further.

The solid residue was acidified with a 2% solution of HCl in water (200 ml) and the solution was then filtered. The solid residue recovered from the filter was washed with water (40 ml). The yield was 29.8 % and comprised 40 % suberin, 35 % betulinol, 25 % phenol and fatty acids.

Comparative example 2 modification of US 2009/0182158 A1, Ex. 1

Outer birch bark (20 g) was added to a solution of NaOH (0,5 N) and IPA (200 ml). The reaction mixture was cooked for 1 hr and then filtered. 200 ml of water was added and the IPA was evaporated at pH 12 yielding a solid residue.

The solid residue was extracted with 2 x 100 ml heptane The heptane phases where combined and evaporated. The yield of betulinol was 2,4 %. The pH of the water phase was adjusted to pH 3 and the solution was then filtered. The yield was 4,3 % of suberin and betulinol. The adding of water resulted in very low yields.

Example 1

Betula verrucosa bark (comprising about 80 w-% dry solids including about 25 w-% product extracts and thereto about 20 w-% water) used as raw material was pre-treated by mechanical log peeling and mechanical chipping and crushing, where after the inner bark was separated from the outer bark by water separation, the water was separated, the material was dried with hot air to a residual humidity below 23% and moved to intermediate storage. The raw material density was from 120 to 150 kg/m^3.

Fig 1 shows a schematic flow diagram of the process. For the hydrolysis 2 the reactor was first loaded with 15 g of the pretreated birch outer bark 1 and a 0,5 N solution of NaOH (3,5 g in 2 ml water), where after 150 ml of IPA (80 w-%, 5:1) was added at almost

boiling temperature. The solid-liquid extraction was continued for 30 minutes at atmospheric pressure (at refluxing temperature at about 80°C). The solvent liquid containing the extracts was then removed from the reactor and the bark residue was mixed 3 again with 2x100 ml of IPA (80 w-%) for 10 minutes at boiling temperature. The reactor was emptied from the washing solvent and the bark was steamed to remove the solvent. The remaining solids where removed from the reactor.

The pH of the liquid phase comprising the solvent liquid from the hydrolysis, the washing solvent as well as the steam mixture was adjusted from alkali to acidic (pH 3) with hydrochloric acid (1N HCl). The same volume of water (50 v-%) (compared to the total amount of liquid from the hydrolysis, washing and steam mixture) was added slowly to the liquid phase (about 10 ml / minute) 4. The extracts precipitated from the liquid phase and the mixture was then pumped to a filter for separation of the precipitated extract 5. The water (40 ml) was pumped to the filter at the same time as the mixture in order to remove extra salts and other impurities of the extract. After precipitation and washing the concentration of the extract was approximately 20 w-%. This slurry was fed into an intermediate evaporation tank for evaporation (at atmospheric pressure and a temperature about 85-90 °C) and concentrated to approximately 60 w-% extract 6. The extract was almost totally free of IPA and contained water. The evaporated gas was distilled 8 and the concentrated extract was pumped to a horizontal Lödige Druvatherm dryer 6 (at about 40 kPa (a) and a temperature about 70-80 °C). Before drying a carrier, i.e. diatomaceous earth in an amount of 40 w-% of the total dry matter was added during constant mixing. The dry matter of the extract was over 80 w-%. The yield 7 of the brownish extract recovered by the method of the invention was 42,4 % and comprised about 26 w-% suberin fatty acids, 58 % betulinol and 16 % phenolic complexes. The solvent (IPA, 80 w-%) was circulated through a distilling colon 8 and further to solvent storage 9. Further as much as possible of the water was reused.

The present invention has been described herein with reference to specific embodiments. It is however clear to those skilled in the art that the process(es) may be varied within the bounds of the claims.

Claims

1. A method for recovering a birch bark extract comprising the following steps:
   a) subjecting birch bark to hydrolysis using a hydrolysis liquid comprising solvent,
   b) separating undissolved bark portions from solvent liquid remaining after the hydrolysis of step a),
   c) providing a liquid phase comprising said solvent liquid,
   d) acidifying said liquid phase,
   e) precipitating extracts from said liquid phase by raising the relative amount of water to between 30 and 70 v-%, more preferably 55 and 65 v-%, most preferably about 60 v-% of water of the total amount of liquids, and
   f) recovering extract.

2. The method according to claim 1, **characterized** in that said undissolved bark portion of step b) is washed with solvent, the solvent is separated and the separated solvent is combined with the solvent liquid of step c) to provide said liquid phase.

3. The method according to claim 1 or 2, **characterized** in that said undissolved bark portion of step b) is steamed to remove solvent, a steam mixture is separated from the bark residue and said steam mixture is combined with the solvent liquid of step c) to provide said liquid phase.

4. The method according to any one of the preceding claims, **characterized** in that said liquid phase is acidified to a pH from pH 4 to pH 2, more preferably from pH 3 to pH 2.

5. The method according to any one of the preceding claims, **characterized** in that said raising of the relative amount of water content during step e) is achieved by adding water and/or by evaporating the solvent from the acidified liquid phase.

6. The method according to claim 5, **characterized** in that 30 and 70 v-%, more preferably 45 and 55 v-%, most preferably about the same volume of water as the volume of the liquid phase is added to said liquid phase.

7. The method according to any one of the preceding claims, **characterized** in that said solvent used for hydrolysis and/or washing is one or more of alcohol; acetone; cyclohexane; ethyl acetate; water or mixtures thereof, preferably alcohol, most preferably ethanol or isopropanol.

8. The method according to any one of the preceding claims, **characterized** in that said birch bark is mechanically processed before said hydrolysis, preferably by log peeling, chipping, crushing, grinding, shredding, milling or any combinations thereof.

9. The method according to any one of the preceding claims, **characterized** in that said recovering of said extract comprises drying and adding a carrier to the extract before said drying.

10. The method according to any one of the preceding claims, **characterized** in that said carrier is diatomaceous earth, preferably added in an amount of 1 to 60 w-%, more preferably 30 to 50 w-%, most preferably about 40 w-% of the total dry matter.

11. An animal feed obtainable by a method according to any one of claims 1 to 10.

12. Use of the birch bark extract of a method according to any of claims 1 to 10 in food, animal feed, pulp, paper and board, pigments and barriers for paper coating.

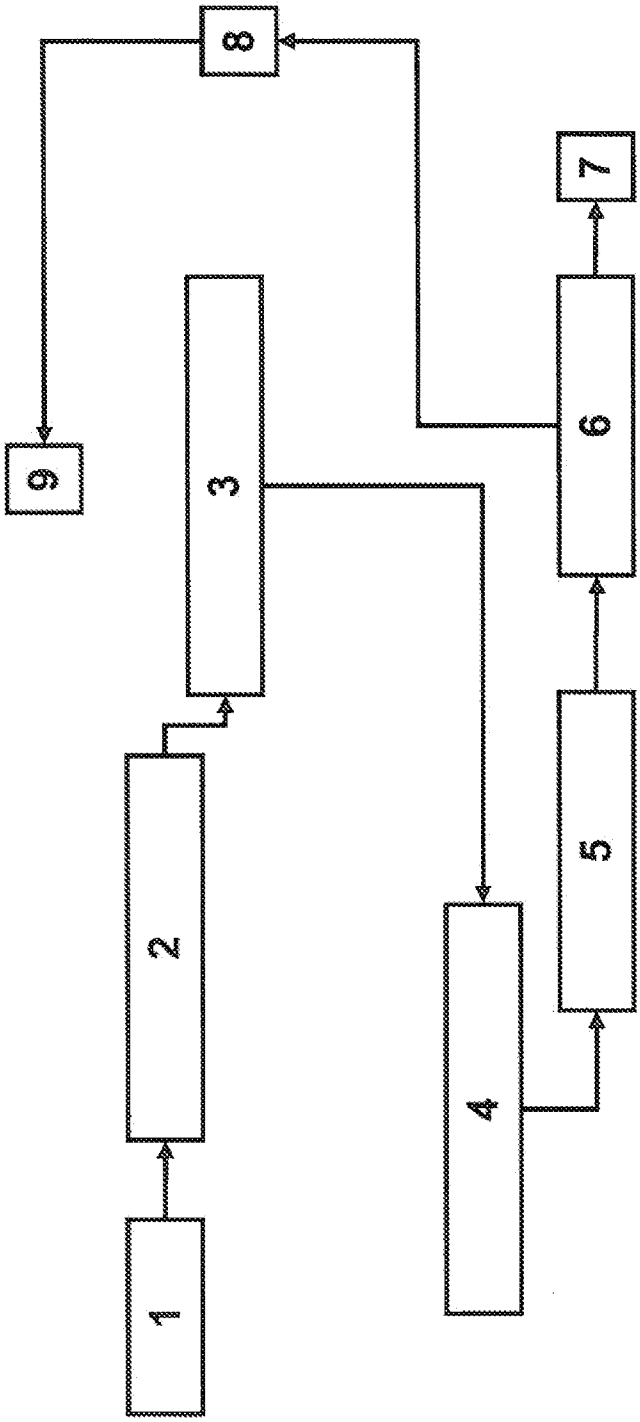

Fig 1