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(54) **METHODS OF ENRICHING ARABINOSE FRACTIONS**

VERFAHREN ZUR ANREICHERUNG VON ARABINOSEFRAKTIONEN

PROCÉDÉS D'ENRICHISSEMENT DE FRACTIONS D'ARABINOSE

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Description

Field of the Invention

[0001] The present invention relates to methods of processing arabinose fractions, especially to methods of enriching arabinose fractions containing, besides arabinose mineral acid and salt. These methods are particularly suitable in the (industrial-scale) production of high-purity crystalline arabinose from crude arabinose extracts produced from plant materials. The present invention also pertains to the enriched arabinose fractions and the crystalline arabinose materials that can be obtained with these methods.

Background of the Invention

[0002] L-Arabinose is a non-caloric sweetener which has taste characteristics similar to sucrose and shows little absorbability. The carbohydrate chemistry of the human body centers around sugars with 'D' configurations. No human enzyme can synthesize or digest sugars of 'L' configurations. The non-enzymatic chemistry and general properties of L- sugars should be essentially identical to their D-counterparts. This makes L-arabinose and the L-counterparts of common sugars such as L-fructose, L-glucose and L-sucrose interesting sweeteners; they should taste like D-sugars yet cannot be metabolized by human enzymes. L-fructose, L-glucose and L-sucrose do not occur naturally. L-arabinose on the other hand can be obtained from natural sources in substantial amounts, which make L-arabinose a very non-nutritive sweetener as well as an important starting material for synthesizing other non-nutritive sweeteners, in particular for synthesizing the L-counterparts of common sugars. L-arabinose also has been proposed as a starting material for producing certain drug substances.

[0003] Arabinose naturally occurs in certain plant derived materials, often as the hemicelluloses arabinan and arabino-galactan. Well-known examples of such plant derived materials include mesquite gum, cherry gum, peach gum, rye and wheat bran, beet pulp and in the wood of coniferous trees. In some of these sources, the content of these hemicelluloses is substantial. For example, 20-30% of the pectic substance in sugar beet is araban. The wood of genus Larix may contain 25% L-araban-D-galactan.

[0004] Although arabinose has valuable uses, currently available processes for isolating it from these plant sources are cumbersome and expensive in practice. Thus the practical utilization of L-arabinose as a food ingredient and/or as a starting material for producing other compounds is still hampered.

[0005] Quite some literature is available regarding the extraction of arabinose from various (natural) polysaccharide materials. The general approach for most of the conventional processes is to use acid conditions for hydrolysing pectin, hemicellulose, xylan and arabinoxylan structures present in these materials. The obtained crude arabinose solutions typically contain a variety of mono-, di-, tri-, oligo- and polysaccharides, as well as most of the added mineral acids as well as a substantial amount of the mineral salts typically present in the raw plant material. These solutions have to be purified in order to render the crystallization of high-purity arabinose feasible.

[0006] The separation of the (mineral) impurities from the arabinose has proven to be a particular challenge. Methods have been proposed in the art that are reasonably effective, but often rely on techniques that hamper industrial-scale production of high-purity (crystalline) arabinose, i.e. in an economically viable manner. It is a particular challenge to develop processes that meet the demand for very high purity and at the same time only rely on techniques that are suitable for industrial scale applications. Most of the processes known to date, at best, provide a compromise between these two requirements.

[0007] An exemplary process for the production and purification of arabinose fractions is described in US 6,506,897. A method is described comprising extraction of a crude arabinose fraction from sugar beet pulp with a strong alkaline solution, followed by hydrolysation with acid to obtain a crude L-arabinose solution, which is subsequently subjected to ion exclusion chromatography (using a cation exchange resin in monovalent metal form as the stationary phase). Crystalline L-arabinose is obtained from the the L-arabinose containing fraction(s) with purities up to 98 % and yields of 10-15 % (based on pulp dry pulp weight). From the practical and economical point of view this process has certain disadvantages, especially because it involves chromatographic separation. In addition, higher degrees of purity will often be desired. Further processes for the production and purification of arabinose fractions are described in WO 2013/152493 and WO 2005/042788.

[0008] There is thus a long felt and still unmet need for economically feasible processes for producing high-purity (crysralline) L-arabinose from crude extracts.

Summary of the Invention

[0009] The present inventors have developed a process that meets this need. The invention, in one aspect, resides in the discovery that mineral acids can efficiently be removed from crude arabinose fractions obtained in 'conventional'

extraction processes, using the subsequent steps of cation exchange treatment and nanofiltration.

[0010] Methods of the invention, more in particular, comprise the steps of treating an arabinose fraction containing arabinose, at least one mineral acid, and at least one metal cation containing compound, using cation exchange treatment, typically aimed at the replacement of metal cations for protons, followed by nanofiltration, typically aimed at the separation of arabinose and mineral acid (anions), yielding a retentate as the enriched arabinose fraction.

[0011] In further embodiments, the invention provides processes of producing high-purity crystalline L-arabinose, comprising the step of producing an enriched arabinose fraction using the method of the invention, and treating it so as to induce crystallization of arabinose.

[0012] In further embodiments, the invention provides processes of producing an arabinose fraction containing arabinose, at least one mineral acid, and at least one metal cation containing compound from crude arabinose extracts, typically derived from plant material, and subsequently subjecting it further enriching it using the method of the invention.

[0013] In further embodiments, the invention pertains the intermediate and end-products obtainable by the methods described herein.

[0014] These and other aspects of the invention will be described in more detail in the following sections.

Detailed Description of the Invention

[0015] A first aspect of the invention concerns a method of enriching and/or purifying an arabinose fraction, said method comprising the consecutive steps of:

a) providing an aqueous liquid comprising an arabinose fraction containing arabinose, at least one mineral acid, and at least one metal cation containing compound;
b) subjecting the aqueous liquid to a treatment resulting in the removal of metal cations, preferably to a treatment selected from cation exchange treatment and electrodialysis;
c) passing the liquid obtained in step b) through a nanofiltration membrane having a molecular weight cut-off value within the range of 150-250 Da;
d) collecting the retentate as the enriched arabinose fraction.

[0016] In accordance with the invention, the term 'arabinose fraction' is used to refer to the arabinose containing fraction that is obtained in a respective step of the process. Hence, the arabinose fraction will contain arabinose, optionally in combination with other solid constituents, as specified throughout this document. The type and (relative) amount of any other constituent of the arabinose fraction may vary, depending on the step of the process in which it is produced, as will be understood by those skilled in the art. For example, a crude arabinose extract obtained from natural (plant) materials will typically contain, besides arabinose, mineral acids and metal cation containing compounds, other monosaccharides, oligosaccharides, proteins, ash, etc. Arabinose fractions in accordance with the invention will typically be dissolved/dispersed (as the case may be) in a liquid phase, typically it may be dissolved/dispersed in water or an aqueous liquid.

[0017] As will be understood by those skilled in the art, based on the foregoing, steps a)-d) as defined above are primarily aimed at separating arabinose from mineral acids and metal cation containing compounds, thereby obtaining an enriched or purified arabinose fraction dissolved in water, from which arabinose can be crystallized.

[0018] Hence, in accordance with the invention, the arabinose fraction provided in step a) contains, besides arabinose, at least one mineral acid, preferably at least one mineral acid selected from the group of nitric acid, hydrochloric acid, sulfuric acid and phosphoric acid, more preferably nitric acid. Typically, the total amount of acid present in the arabinose fraction of step a) is within the range of 40-150 % (w/w), based on the total dry weight of the arabinose fraction, preferably within the range of 50-145 % (w/w), more preferably within the range of 60-140 % (w/w).

[0019] In accordance with the invention, the arabinose fraction provided in step a) contains, besides arabinose, at least one metal cation containing compound, preferably at least one alkali metal cation containing compound or earth alkali metal cation containing compound, more preferably a Ca^{2+}, Mg^{2+}, Na^{+} or K^{+} containing compound. Typically, the metal cation containing compound is water soluble. More preferably the metal cation containing compound has a water solubility of at least 100 g/l at a temperature of 20°C and a pH of 7. Most preferably, the arabinose fraction contains a metal cation in nitrate salt form. Typically, the total amount of metal cation containing compound in the arabinose fraction of step a) is within the range of 5-40 % (w/w), based on the total dry weight of the arabinose fraction, preferably within the range of 10-30 % (w/w), more preferably within the range of 15-25 % (w/w).

[0020] The (relative) amount of arabinose in the arabinose fraction provided in step a) is not particularly limited. The present method will allow for the enrichment of the arabinose fraction regardless of the initial arabinose amount. Yet, in preferred embodiments of the invention, the amount of arabinose in the arabinose fraction is at least 10 % (w/w), based on the total dry weight of the arabinose fraction, more preferably at least 20 % (w/w), more preferably at least 25 % (w/w), more preferably at least 30 % (w/w), most preferably at least 35 % (w/w).

[0021] Typically, the arabinose fraction provided in step a) has a combined level of oligosaccharides of below 20 % (w/w), based on total dry weight of the arabinose fraction, more preferably below 15 % (w/w), more preferably below 10 % (w/w), more preferably below 7.5 % (w/w), more preferably below 6 % (w/w), most preferably below 5 % (w/w).

[0022] Typically, in accordance with the invention, the arabinose provided in step a) fraction will be in the form of an aqueous liquid containing the solid constituents in the (relative) amounts as described herein, in combination with water. The amount of water can vary, as will be understood by those of average skill in the art, depending on the processing steps applied to produce the arabinose fraction. In accordance with the invention, it is preferred however that the aqueous liquid as provided in step a) contains a total level of dissolved solids within the range of 0.25-20 % (w/v), preferably within the range of within the range of 0.5-10 % (w/v), more preferably within within the range of 1-5 % (w/v).

[0023] In an embodiment of the invention, in step b), the aqueous liquid provided in step a) is subjected to cation exchange treatment by contacting it with a protonated cation exchange resin, in order to replace the metal cations present in said aqueous liquid with protons. As will be immediately recognized by those of average skill in the art, this process is distinct from chromatographic separation methods using ion exchange resin as the stationary phase, in that the present method does not rely on on differential partitioning between a mobile phase and a stationary phase. Instead, in accordance with the invention, step b) is performed by combining in an open or closed system, typically in a batch-wise fashion, the aqueous liquid and the protonated cation exchange resin, resulting in displacement of protons initially bound to the resin with metal cations initially present in the aqueous liquid, thereby effectively converting the metal cation compounds to the corresponding acids. For ease of reference, the ion exchange (IE) treated liquid, comprising the arabinose fraction, is also referred to herein as the IE-treated liquid or IE-treated extract.

[0024] In an embodiment of the invention, a process as defined herein before is provided wherein step b) comprises:

b1) contacting the aqueous liquid with a protonated cation exchange resin; and
b2) separating the aqueous liquid from the cation exchange resin.

[0025] In an embodiment of the invention, the cation exchange resin is selected from the group consisting of strong acid cation exchange (SAC) resins. Suitable SAC resins for example include sulfonic acid substituted polystyrene cross-linked with divinyl benzene. Ion exchange resins are typically provided in the form of solid macroporous particles or beads. Commercially available SAC exchange resins of the macroporous type include, for example, Lewatit SCP 118, Lewatit SCP 108, Amberlyst A15 and Amberlyst A35. Other strong acid ion exchange resins include Duolite C20, Duolite C26, Amberlite IR-120, Amberlite 200, Dowex 50, Lewatit SPC 118, Lewatit SPC 108, K2611, K2621, OC 1501. Amberlyte, Amberlyst, Amberjet Duolite, and DOWEX are trademarks of the Dow Chemical Company. Lewatit is a trademark of the Lanxess Company.

[0026] The ion exchange treatment can be performed in any suitable manner known those skilled in the art. In an embodiment of the invention, step b) comprises producing a slurry by combining an amount of cation exchange resin in protonated form and the aqueous liquid and allowing for the exchange of metal cations between the SAC resin and the aqueous liquid to take place. In another embodiment of the invention, step b1) comprises providing a packed column of the ion exchange resin in protonated form, as defined herein, and passing the aqueous liquid over said column. In an embodiment of the invention, the aqueous liquid is passed over the column at a flow rate of 1-4 bed volumes per hour (BV/h), more preferably 2-3 BV/h. In an embodiment of the invention, the packed column has a height of at least 1 meter. In an embodiment of the invention, step b1) is performed at ambient temperature, preferably at 20-25°C, and ambient pressure. In accordance with the invention, step b1) is typically performed in a batch-wise fashion.

[0027] As defined in the foregoing, step b2) comprises collecting the IE treated liquid. As will be understood by those skilled in the art, in an embodiment step b1) comprises producing a slurry by combining an amount of cation exchange material in protonated form and the aqueous liquid comprising the arabinose fraction, followed by a step of separating the solid ion exchange material from the liquid, using any suitable conventional solid-liquid separation technique. In another embodiment, step b1) comprises passing the aqueous liquid over a packed column of ion exchange material and step b2) comprises collecting the eluate. After use, the ion exchange material can be regenerated with a strong acid, such as hydrochloric acid so as to replace all metal cations bound to the resin with protons, following which the ion exchange material can be re-used to treat a subsequent batch of aqueous liquid containing an arabinose fraction.

[0028] In an embodiment of the invention, in step b), the aqueous liquid provided in step a) is subjected to electrodialysis treatment. Electrodialysis is a separation method for use with ionic solutions. It uses an electric field which generates a motive force for the migration of ions in solution and ion-permeable membranes which ensure the selectivity of the ion migration and which also allow part of the ionic charge of the solutions to be removed. Suitable electrodialysis units that can be utilized in the method of the present invention are known to those of average skill in the art and it is within the normal capabilities of those skilled in the art to employ them in an effective manner. For ease of reference, the electrodialysis (ID) treated liquid, comprising the arabinose fraction, is also referred to herein as the ID-treated liquid or ID-treated extract. According to the invention, the IE- or ID-treated aqueous liquid is subjected to a nanofiltration treatment.

[0029] As defined herein before, step c) of the present process comprises a nanofiltration treatment. The term "nano-

filtration" refers to a form of pressure driven filtration that uses semipermeable membranes of pore size typically in the 0.001-0.1 μm range, to separate different fluids or ions. Such methods are well-known in the art. In accordance with the invention, step c) comprises contacting the aqueous liquid with a semi-permeable membrane while applying a pressure difference across the membrane. A major portion of the mineral acids and salts pass through the membrane with a portion of the water in a permeate stream and are thereby concentrated in the permeate stream. The major part of the arabinose does not pass through the membrane (i.e. is "rejected") resulting in a concentrated retentate stream. For ease of reference, the retentate stream from the nanofiltration step, comprising the enriched and/or purified arabinose fraction, is also referred to herein as the enriched liquid/extract or purified extract/liquid.

[0030] Nanofiltration membranes are generally classified based on the molecular weight cut-offs. Generally, the largest pore size that will provide at least 95%, 96%, 97%, 98%, or 99% arabinose retention is preferred. Nanofiltration membranes suitable for the present invention typically have a molecular weight cut-off (MWCO) within the range of 150 to 250 Da, as defined herein before. In a preferred embodiment of the invention, step c) is performed using a nanofiltration membrane having a molecular weight cut-off value within the range of 160-225 Dalton, more preferably within the range of 170-200 Dalton, more preferably within the range of 175-190 Dalton, e.g. about 180 Dalton.

[0031] Different types of nanofiltration membranes are (commercially) available, made of ceramic, semi-conducting or polymeric materials, including for example aluminium-oxide, zirconium oxide, titanium oxide or mixtures thereof, siliciumnitride or other silicium based compounds or mixtures thereof, polysulphones, fluoropolymers, cellulose, polyolefin resins and polyethersulphones. In embodiment of the invention, it is preferred that the porous nanofiltration membrane is a polymeric porous membrane, preferably and acid stable polymeric porous membranes. Polymeric membranes with stability toward acids are known by those skilled in the art. Examples of polymers that are relatively stable towards acids and can be used to prepare membranes include polyolefins such as, for example, polyethylene and polypropylene, polyvinylidene flouride, polysulfones, polyethersulfone, and polyether ketones.

[0032] With regard to the filtration mode and/or the configuration of the filter module, the invention is not particularly limited. Both the direct Flow Filtration (DFF) mode and the Tangential Flow Filtration (TFF) mode may be suitable for the purposes of the invention. Examples of different filter modules known in the art that may be used in one of these filtration modes include hollow fibre modules, spiral wound modules, tubular modules, and plate modules. In an embodiment of the invention, it is preferred that a spiral wound module is used, e.g. a spiral wound module Type AMS 3012 from AMS - Tel Aviv - Israel.

[0033] Conditions to be applied during nanofiltration will depend on a number of variables as will be understood by the skilled person. It is within the skills of the trained professionals to carry out and optimize the process depending on the specific circumstances. In an embodiment of the invention, a flux of 5-50 l/m^2h is applied, preferably 10-40 l/m^2h, more preferably 20-30 l/m^2h. In an embodiment of invention, the pressures applied result in a transmembrane pressure within the range of 10-50 bar, preferably 15-45 bar, more preferably 20-40 bar. For the nanofiltration process, the temperature is typically kept within the range of 10-60 °C, preferably within the range of 20-25 °C.

[0034] In an embodiment of the invention, the nanofiltration is operated in diafiltration mode, to further reduce the level of mineral acids and salts in the arabinose fraction. In this case, the arabinose fraction is first concentrated until a given optimal value of the concentration factor (CF), and then the nanofiltration proceeds with the addition of water to the retentate.

[0035] In an embodiment of the invention, step c) comprises diafiltration in discontinuous mode. In discontinuous diafiltration, sequential cycles of dilution and concentration are performed. Typically, in an embodiment of the invention, step d) comprises the steps of c1) concentrating the sample by nanofiltration; c2) diluting the sample with water to a predetermined volume and c3) concentrating the sample by nanofiltration, e.g. back to the volume obtained in step c1). Steps c2) and c3) may be repeated until the unwanted mineral acids and salts are removed to a sufficient degree. Each subsequent dilution removes more of the mineral acids and salts. It may be advantageous to perform multiple cycles of steps c2) and c3) to achieve the desired results, e.g. up to 15 cycles. In some embodiments, it is preferred to perform at least 1, at least 2, at least 3 or at least 4 cycles.

[0036] In an embodiment of the invention, step c) comprises diafiltration in continuous mode. Continuous diafiltration (also referred to as constant volume diafiltration) involves washing out the original buffer salts (or other low molecular weight species) in the retentate (sample) by adding water or a new buffer to the retentate at the same rate as filtrate is being generated. As a result, the retentate volume and product concentration does not change during the diafiltration process, while the mineral acids and salts will be washed out. Typically, in an embodiment of the invention, step c) comprises continuous mode diafiltration, typically comprising the addition of liquid, typically water, to the retentate side while forcing liquid through the nanofiltration membrane, thereby keeping the volume of liquid containing the arabinose fraction at a predetermined value, e.g. at the original volume. The amount of mineral acids and salts removed is related to the filtrate volume generated, relative to the original retentate volume. The filtrate volume generated is usually referred to in terms of "diafiltration volumes". A single diafiltration volume (DV) is the volume of retentate when diafiltration is started. For continuous diafiltration, liquid is typically added at the same rate as filtrate is generated. When the volume of filtrate collected equals the starting retentate volume, 1 DV has been processed. In accordance with an embodiment

of the the invention, step d) comprises diafiltration in continuous mode, as described herein, wherein at least 2 DV, at least 3 DV or at least 4 DV is processed.

[0037] As mentioned herein above, in an embodiment of the invention, the enriched or purified arabinose fraction can suitably be used for producing high-purity arabinose by crystallization. Embodiments are however also envisaged wherein the retentate obtained in step d) is subjected to one or more additional treatments before performing the crystallization step as defined herein, which additional treatments are typically aimed at the removal of (traces of) certain impurities, especially those that affect the arabinose crystallization. These optional treatments are herein collectively referred to as 'polishing treatments'. Particularly advantageous polishing treatments include anion exchange treatment, yeast fermentation and treatment with active carbon. For ease of reference, the arabinose fraction obtained by polishing of the retentate obtained in step d), is also referred to herein as the polished retentate.

[0038] Hence, in an embodiment of the invention, a method is provided comprising the steps a)-d) as defined herein, said method further comprising the step of:

e) subjecting the retentate obtained in step d) to one or more polishing treatments, preferably to one or more polishing treatments selected form (i) Anion exchange treatment; (ii) fermentative treatment; and (iii) active carbon treatment.

[0039] Anion exchange treatment, in accordance with the invention, is primarily aimed at the removal of residual (mineral) acid and typically comprises contacting the liquid retentate with an OH^- loaded anion exchange resin and can be performed by combining in an open or closed system, typically in a batch-wise fashion, the liquid retentate and the anion exchange resin, resulting in displacement of OH^- initially bound to the resin with mineral acid anions initially present in the retentate, thereby effectively removing the mineral acids. In an embodiment of the invention, the anion exchange resin is selected from the group consisting of weak base, medium base and strong base anion exchange resins, preferably from the group of medium base anion exchange resins. Suitable resins for example include polystyrene resins with bound tertiary and/or quaternary ammonium groups. These resins are typically provided in the form of solid macroporous particles or beads. Anion exchange resin suitable for use in accordance with the invention are commercially available, such as Bayer type S 4268 type resin.

[0040] The anion exchange treatment can be performed in any suitable manner known those skilled in the art, such as by passing the retentate liquid over a packed column of the anion exchange resin material. In an embodiment of the invention, the retentate liquid is passed over the column at a flow rate of 1-4 bed volumes per hour (BV/h), more preferably 2-3 BV/h. In an embodiment of the invention, the packed column has a height of at least 0.5 meter. In an embodiment of the invention, anion exchange treatment is performed at ambient temperature, preferably at 20-25°C, and ambient pressure.

[0041] Fermentative treatment, in accordance with the invention, is primarily aimed at the removal of residual monosaccharides such as glucose, mannose and galactose, in particular galactose, and typically comprises inoculating the retentate liquid, optionally after it has been subjected to anion exchange treatment, with a microorganism capable of consuming said monosccharides and incapable of consuming and/or converting arabinose, followed by incubation of the inoculated liquid retentate under conditions favorable to the growth and development of said microorganism, for a period sufficient to reduce the content of the aforementioned monosaccharides. In an embodiment of the invention, the pH of the liquid retentate is adjusted to a value within the range of 4-5, preferably within the range of 4.3-4.7, before inoculation. In an embodiment of the invention, the mircroorganism is a yeast strain, preferably a strain selected from the genus *Saccharomyces,* preferably selected from *S. cerevisae* and *S. uvarum* most preferably *S. cerevisae.* Suitable commercially available preparations are also sometimes referred to as 'baker's yeast', 'brewer's yeast', 'distillers yeast'and 'wine yeast'. An example of a commercially available yeast that is particularly suitable for use in accordance with the invention is Fermipan Brown (AB Mauri (UK) Ltd). In an embodiment of the invention, the inoculated liquid retentate is incubated at a temperature within the range of 25-35 °C, preferably within the range of 27-33 °C, for a period of 24-60 hours, preferably 36-54 hours. Following incubation, a standard solid-liquid separation step is typically applied in order to separate the solid biomass (mainly yeast cells) from the liquid, such as by microfiltration. In an embodiment the ferment is also treated with active carbon, in which case the solid-liquid separation is conveniently done after said active carbon treatment.

[0042] Active carbon treatment, in accordance with the invention, is primarily aimed at the removal of low MW organic substances that tend to affect the colour, taste and/or flavor of the products eventually produced. Active carbon treatment typically involves the addition of an effective amount of active carbon, typically in particulate/powder form, to the liquid retentate, which may have undergone any further polishing treatment as described here above, and allowing the active carbon to absorb at least a fraction of the low MW organic substances. An example of a commercially available active carbon product that may suitably be used in accordance with the invention is type CN1 from Norit. The active carbon is typically applied in an amount within the range of 0.5-5 g/l, preferably 1-3 g/l. In an embodiment of the invention, the mixture is kept for a period of 0.5-2 hours, preferably 0.75-1.5 hours, typically under gentle agitation, such as stirring, at ambient temperature. Following this treatment, a standard solid-liquid separation step is typically applied in order to separate the active carbon particles from the liquid, such as by microfiltration

[0043] In an embodiment of the invention, a method is provided as defined above, comprising the step of:

e) subjecting the retentate obtained in step d) to the consecutive polishing treatments of (i) anion exchange treatment; (ii) fermentative treatment; and (iii) active carbon treatment.

[0044] The polished retentate obtained following step e) as described here above, can suitably be used for producing high-purity arabinose by crystallization.

[0045] In an embodiment of the invention, a method of producing crystalline arabinose is provided, said method comprising the steps a)-d) or a)-e), as defined herein, said method further comprising the step of:
f) inducing crystallization of arabinose from the retentate obtained in step d) or the polished retentate obtained in step e).

[0046] The term "crystallization", as used herein, refers to any process for the formation of solid crystals of a solute from a saturated or supersaturated solution.

[0047] The crystallization may be carried out by any conventional crystallization methods known in the art. Suitable examples of crystallization methods include: a cooling crystallization method, wherein the temperature of the arabinose-containing liquid is lowered whereby the arabinose precipitates; a concentration crystallization method in which the solvent is volatilized from the solution, for example, by heating and/or a pressure reduction, to heighten the arabinose concentration of the arabinose-containing liquid and thereby precipitate the arabinose; a poor-solvent crystallization method in which a third ingredient (poor solvent) which lowers the solubility of the arabinose is added to the arabinose-containing liquid to precipitate the arabinose; and a method which includes a combination of these.

[0048] In an embodiment of the invention, step f) comprises processing the retentate into a saturated or supersaturated solution of arabinose, exposing the solution to conditions that permit crystallization, and harvesting the crystals so obtained.

[0049] In an embodiment of the invention step f) comprises the steps of:

f1) evaporating water from the (polished) retentate obtained in step d) or e), e.g. under reduced pressure and/or increased temperature;
f2) cooling the concentrated retentate to induce crystallization of the arabinose;
f3) collecting the crystalline arabinose material.

[0050] During step f1) the pressure is typically within the range of 0.05-0.5 bar, preferably 0.1-0.30bar, more preferably 0.18-0.22 bar. The temperature is typically kept within the range of 50-85 °C, preferably within the range of 60-70 °C. more preferably within the range of 63-67 °C.

[0051] The temperature of the arabinose-containing liquid is subsequently lowered to induce crystallization (hereinafter, that temperature is often referred to as crystallization temperature). The crystallization temperature during step f2) is typically within the range of 5-40 °C, preferably within the range of 10-30 °C. more preferably within the range of 15-25 °C. In cooling crystallization processes the rate of cooling may also affect the result. In an embodiment of the invention, it is preferred that the arabinose-containing liquid is cooled to the crystallization temperature over 6-48 hours, more preferably 12-36 hours, morst preferably 18-24 hours and then aged at the crystallization temperature for 6-48 hours, more preferably 12-36 hours, most preferably 18-24 hours. In this operation, the rate of cooling the arabinose-containing liquid is usually preferably 0.05-2 °C/min, more preferably 0.1-1.5 °C/min, even more preferably 0.2-1 °C/min.

[0052] The solution may be seeded with seed crystals of arabinose. In an embodiment of the invention, pulverized crystals of arabinose in a dry form or suspended in a crystallization solvent are added to the saturated or supersaturated liquid, e.g. during step f2) as described above.

[0053] After step f2), the arabinose crystals are collected, for example by filtering the crystallization liquid. The filtration can be carried out with traditional centrifuges or filters. The filtration cake may be washed with the crystallization solvent and dried. Drying can be carried out for example at a temperature between 30 and 90 °C by traditional methods.

[0054] Crystals of arabinose with a high purity are obtained. The crystallization typically provides crystalline arabinose having a purity of over 99%. The melting point of the obtained crystalline material is typically within the range of 155-163 °C.

[0055] As will be understood by those of average skill in the art, the arabinose fraction treated in accordance with the invention, preferably originates from a natural (plant) source. Crude arabinose extracts obtained from natural (plant) sources will often contain, besides arabinose, mineral acids and salts, a number of other mono-saccharides, di-saccharides, tri-sacharides, oligosaccharides, polysaccharides, proteins, ashes, etc. Such crude extracts are therefore preferably subjected to one or more pre-treatment steps. Such pre-treatment steps may include, for example, ultrafiltration and/or nanofiltration.

[0056] In an embodiment of the invention, a method as defined herein is provided, wherein step a) comprises:

- providing an aqueous liquid comprising an arabinose fraction containing arabinose, at least one mineral acid, at least one metal cation containing compound and at least one oligosaccharide component;
- treating said liquid by passing it through a nanofiltration membrane having a molecular weight cut-off value within the range of 500-3000 Da and collecting the permeate containing the arabinose fraction.

[0057] With this treatment a retentate is obtained comprising the olicho-saccarides and a permeate enriched in arabinose, typically also comprising the mineral acids and salts as well as other monosaccharides, disaccharides, trisaccharides and small oligosaccharides. For ease of reference, the permeate obtained after nanofiltration (NF) pre-treatment, comprising the arabinose fraction, is also referred to herein as the NF-treated liquid or NF-treated extract.

[0058] Membranes suitable for the NF pre-treatment include nanofiltration membranes having a molecular weight cut-off (MWCO) of 500 to 3000 Da, more preferably 750-2000 Da, most preferably 900-1500, e.g. an MWCO or around 1000.

[0059] Different types of nanofiltration membranes are (commercially) available, made of ceramic, semi-conducting or polymeric materials, including for example aluminium-oxide, zirconium oxide, titanium oxide or mixtures thereof, siliciumnitride or other silicium based compounds or mixtures thereof, polysulphones, fluoropolymers, cellulose, polyolefin resins and polyethersulphones. In embodiment of the invention, it is preferred that the nanofiltration membrane is a polymeric porous membrane, preferably and acid stable polymeric porous membranes. Polymeric membranes with stability toward acids are known by those skilled in the art. Examples of polymers that are relatively stable towards acids and can be used to prepare membranes include polyolefins such as, for example, polyethylene and polypropylene, polyvinylidene flouride, polysulfones, polyethersulfone, and polyether ketones.

[0060] With regard to the filtration mode and/or the configuration of the filter module, the invention is not particularly limited. Both the direct Flow Filtration (DFF) mode and the Tangential Flow Filtration (TFF) mode may be suitable for the purposes of the invention. Examples of different filter modules known in the art that may be used in one of these filtration modes include hollow fibre modules, spiral wound modules, tubular modules, and plate modules. In an embodiment of the invention, it is preferred that a tubular module is used, e.g. a multichannel ceramic type module from Tami-France having a hydraulic diameter of 3.5 mm and a length of 1200 mm.

[0061] Conditions to be applied during the nanofiltration pre-treatment will depend on a number of variables as will be understood by the skilled person. It is within the skills of the trained professionals to carry out and optimize the process depending on the specific circumstances. In an embodiment of the invention, a flux of 5-50 l/m^2h is applied, preferably 10-40 l/m^2h, more preferably 20-30 l/m^2h. In an embodiment of invention, the pressures applied result in a transmembrane pressure within the range of 2-30 bar, preferably 3-20 bar, more preferably 4-10 bar. For the nanofiltration process, the temperature is typically kept within the range of 20-80 °C, preferably within the range of 40-60 °C.

[0062] In an embodiment of the invention, the nanofiltration pre-treatment is operated in diafiltration mode in continuous or discontinuous mode. In an embodiment of the invention, the pre-treatment comprises diafiltration in discontinuous mode, wherein sequential cycles of dilution and concentration are performed. Typically, in an embodiment of the invention, the pre-treatment comprises the steps of concentrating the aqueous liquid by nanofiltration; diluting the retentate with water to a predetermined volume and concentrating the diluted retentate by nanofiltration, e.g. back to the original volume. It may be advantageous to perform multiple cycles to achieve the desired result, e.g. up to 15 cycles. In some embodiments, it is preferred to perform at least 1, at least 2, at least 3 or at least 4 cycles. In an embodiment of the invention, the pre-treatment comprises diafiltration in continuous mode, wherein water is added to the retentate side while forcing liquid through the nanofiltration membrane, thereby keeping the volume of liquid containing the arabinose fraction at a predetermined, preferably constant, value, e.g. at the original volume. In accordance with an embodiment of the the invention, step d) comprises diafiltration in continuous mode, as described herein, wherein at least 2 DV, at least 3 DV or at least 4 DV is processed.

[0063] In an embodiment of the invention, a method as defined herein is provided, In an embodiment of the invention, a method as defined herein is provided, wherein step a) comprises:

- providing an aqueous liquid comprising an arabinose fraction containing arabinose, at least one mineral acid, at least one metal cation containing compound, at least one oligosaccharide component and pectin, such as a crude arabinose extract obtained from a plant material or plant pulp, e.g. by acid extraction;
- treating said liquid by passing it through an ultrafiltration membrane having a molecular weight cut-off value within the range of 5 - 50 KDa, and collecting the permeate as the arabinose fraction; and
- treating said permeate by passing it through a nanofiltration membrane having a molecular weight cut-off value within the range of 500-3000 Da and collecting the permeate containing the arabinose fraction, as defined herein before.

[0064] With the ultrafiltration treatment a retentate is obtained containing mainly pectin and a permeate enriched in arabinose, and typically also comprising mineral acids and salts as well as other monosaccharides, disaccharides, trisaccharides and oligosaccharides. For ease of reference, the permeate obtained after ultrafiltration (UF) pre-treatment, comprising the arabinose fraction, is also referred to herein as the UF-treated liquid or UF-treated extract.

[0065] Ultrafiltration membranes suitable for the present invention typically have a molecular weight cut-off (MWCO) of 5 - 50 kDa, more preferably 10-30 kDa, most preferably 12-20, e.g. an MWCO of around 15 kDa.

[0066] Different types of ultrafiltration membranes are (commercially) available, made of ceramic, semi-conducting or polymeric materials, including for example aluminium-oxide, zirconium oxide, titanium oxide or mixtures thereof, silici-

umnitride or other silicium based compounds or mixtures thereof, polysulphones, fluoropolymers, cellulose, polyolefin resins and polyethersulphones. In embodiment of the invention, it is preferred that the porous ultrafiltration membrane is a polymeric porous membrane, preferably and acid stable polymeric porous membranes. Polymeric membranes with stability toward acids are known by those skilled in the art. Examples of polymers that are relatively stable towards acids and can be used to prepare membranes include polyolefins such as, for example, polyethylene and polypropylene, polyvinylidene flouride, polysulfones, polyethersulfone, and polyether ketones.

[0067] With regard to the filtration mode and/or the configuration of the filter module, the invention is not particularly limited. Both the direct Flow Filtration (DFF) mode and the Tangential Flow Filtration (TFF) mode may be suitable for the purposes of the invention. Examples of different filter modules known in the art that may be used in one of these filtration modes include hollow fibre modules, spiral wound modules, tubular modules, and plate modules. In an embodiment of the invention, it is preferred that a tubular module is used, e.g. a multichannel ceramic type module from Tami-France having a hydraulic diameter of 3.5 mm and a length of 1200 mm.

[0068] Conditions to be applied during the ultrafiltration pre-treatment will depend on a number of variables as will be understood by the skilled person. It is within the skills of the trained professionals to carry out and optimize the process depending on the specific circumstances. In an embodiment of the invention, a flux of 5-50 l/m^2h is applied, preferably 10-40 l/m^2h, more preferably 20-30 l/m^2h. In an embodiment of invention, the pressures applied result in a transmembrane pressure within the range of 2-30 bar, preferably 3-20 bar, more preferably 4-10 bar. For the ultrafiltration process, the temperature is typically kept within the range of 20-80 °C, preferably within the range of 40-60 °C.

[0069] In an embodiment of the invention, the ultrafiltration pre-treatment is operated in diafiltration mode in continuous or discontinuous mode. In an embodiment of the invention, the pre-treatment comprises diafiltration in discontinuous mode, wherein sequential cycles of dilution and concentration are performed. Typically, in an embodiment of the invention, the pre-treatment comprises the steps of concentrating the aqueous liquid by ultrafiltration; diluting the retentate with water to a predetermined volume and concentrating the diluted retentate by ultrafiltration, e.g. back to the original volume. It may be advantageous to perform multiple cycles to achieve the desired result, e.g. up to 15 cycles. In some embodiments, it is preferred to perform at least 1, at least 2, at least 3 or at least 4 cycles. In an embodiment of the invention, the pre-treatment comprises diafiltration in continuous mode, wherein water is added to the retentate side while forcing liquid through the ultrafiltration membrane, thereby keeping the volume of liquid containing the arabinose fraction at a predetermined, preferably constant, value, e.g. at the original volume. In accordance with an embodiment of the the invention, step d) comprises diafiltration in continuous mode, as described herein, wherein at least 2 DV, at least 3 DV or at least 4 DV is processed.

[0070] In an embodiment of the invention, a method as defined herein is provided, wherein step a) comprises the consecutive steps of:

a1) providing an arabinose containing plant material, preferably a plant pulp, more preferably a spent sugar beet pulp;
a2) placing a first quantity of the plant material provided in a1) in a reactor with an aqueous mineral acid solution, preferably under agitation and/or heating;
a3) extracting liquid from the mixture obtained in step a2) by solid-liquid separation;
a4) pre-treating the extracted liquid by passing it through an ultrafiltration membrane having a molecular weight cut-off value within the range of 5 - 50K Da and collecting the permeate, as described herein before; and
a5) pre-treating the permeate by passing it through a nanofiltration membrane having a molecular weight cut-off value within the range of 500 - 3000 Da and collecting the permeate, as described herein before.

[0071] As explained herein before, the process of the invention is particularly suitable for the enrichment of arabinose fractions obtained from a natural source. Arabinose can be obtained from a broad range of natural sources, including by-products obtained during processing of agricultural or forestry raw materials. Typical examples of such by-products are e.g. cereal straw, cereal bran, corn stover, corn cobs, bagasse, sugarbeet pulp, almond shells, coconut shells, chicory, gum arabic or other ligno-cellulosic by-products. The respective by-products as well as the feedstock used in the respective processes, are collectively referred herein as 'arabinose containing plant material'.

[0072] Particularly preferred is the use of fresh, pressed-out sugar beet pulp from which the sugars have been extracted and which has a dry solids content of 10-50 wt.%, preferably 20-30 wt.%, for example approximately 25 wt.%. Sugar beet pulp is the production residuum from the sugar beet industry. More specifically, sugar beet pulp is the residue from the sugar beet after the extraction of sucrose there from. This material is also referred to as 'spent sugar beet pulp'. Sugar beet processors often dry the pulp. The dry sugar beet pulp can be referred to as 'sugar beet shreds' or 'sugar beet cosettes'. Additionally, the dry sugar beet pulp or shreds can be formed and compressed to produce "sugar beet pellets". These materials may also be used as the starting material, in which case step a1) will comprise suspending the dry sugar beet pulp material in an aqueous liquid, typically to the afore-mentioned dry solids contents. Preferably however, fresh wet sugar beet pulp is used as the staring material.

[0073] Another preferred starting material is ensilaged vegetable pulp, especially ensilaged sugar beet pulp. As used

herein, the term "ensilage" refers to the process of storing vegetable materials in a moist state under conditions resulting in acidification caused by anaerobic fermentation of carbohydrates present in the materials being treated. Ensilage is carried out according to known methods with pulps preferably containing 15 to 35% of dry matter. Ensilage of sugar beets is continued until the pH is within the range of 3.5-5. It is known that pressed beet pulps may be ensilaged to protect them from unwanted decomposition. This process is most commonly used to protect this perishable product, the other alternative being drying to 90% dry matter. This drying has the disadvantage of being very energy-intensive. The fermentation process starts spontaneously under anaerobic conditions with the lactic acid bacteria being inherently present. These microorganisms convert the residual sucrose of the pressed beet pulp to lactic acid, causing a fall in the pH.

[0074] In an embodiment of the invention, the arabinose containing plant material or pulp is washed in a flotation washer in order to remove sand and clay particles before subjecting it to the acid treatment.

[0075] In step a2) of the method, the water-soluble pectin material is extracted from the arabinose containing plant material by acid catalyzed hydrolysis. For ease of reference, the liquid obtained in accordance with step a2), comprising the plant material and an acid, is also referred to herein as the hydrolysis mixture.

[0076] In an embodiment of the invention, a method as defined herein is provided, wherein step a2) comprises placing the plant material in a reactor with an aqueous solution of a mineral acid selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid or phosphoric acid. In a preferred embodiment of the invention, step a2) comprises placing the plant material in a reactor with an aqueous solution of nitric acid.

[0077] In an embodiment of the invention, a method as defined herein is provided, wherein step a2) comprises placing the plant material in a reactor with an aqueous solution of a mineral acid in amounts resulting in an acid concentration of 0.5-4 % (w/v), preferably 0.75-3 % (w/v), more preferably 1-2 (w/v).

[0078] In an embodiment of the invention, a method as defined herein is provided, wherein step a2) comprises placing the plant material in a reactor with an aqueous solution of a mineral acid in amounts resulting in a level of sugar beet solids of 5-25 wt.%, based on the total weight of the obtained slurry, preferably 7-15 wt.%, more preferably 8-10 wt.%.

[0079] In an embodiment of the invention, the treatment according to step a2) comprises mixing the arabinose containing plant material with the aqueous solution of a mineral acid and heating the mixture accordingly obtained to a temperature within the range of 40-100 °C for a period of at least 10 minutes, preferably at least 20 minutes, more preferably at least 30 minutes. The use of relatively low temperatures in the present chemical process allows the plant material to be processed with the use of less energy and therefore at a lower cost than methods known in the art employing higher temperatures. Yet, in accordance with certain embodiments, the mixture may be heated to at least 60°C, at least 70°C, at least 80°C or at least 90°C. Preferably, the mixture is heated to less than 100°C, preferably less than 90°C, more preferably less than 85 °C. As will be appreciated by those skilled in the art, the use of higher temperatures, within the indicated ranges, will reduce the processing times and *vice versa*. It is a matter of routine optimization to find the proper set of conditions in a given situation. In an embodiment of the invention, a method as defined herein is provided, wherein step a2) comprises placing the spent plant material in a reactor with an aqueous mineral acid solution and heating the solution to a temperature within the range of 50-100 °C, for a period of time within the range of 30- 240 minutes, preferably under agitation. In an embodiment, step a2) comprises heating the mixture to a temperature of 70-90°C for 120-240 minutes, for example to a temperature of approximately 80 °C for 180 minutes. In an embodiment of the invention, the mixture is stirred or agitated during step a2).

[0080] Step a2) is followed by a step a3) of extracting an aqueous liquid containing the arabinose fraction. For ease of reference, the liquid obtained in accordance with step a3) , comprising the arabinose fraction, is also referred to herein as the crude extract.

[0081] In an embodiment of the invention, a method as defined herein is provided, wherein step a3) comprises taking the hydrolysis mixture obtained in step a2) from the reactor and subjecting it to a solid-liquid separation process, preferably filtration, centrifuging and/or decantation and collecting the extracted liquid as the arabinose fraction. In one preferred embodiment of the invention, the hydrolysis mixture is subjected to filtration, e.g. in a chamber filter press, during which extracted liquid is collected as the arabinose fraction. As will be understood by those skilled in the art, it is possible to incorporate multiple processing steps in order to achieve optimal results. For example, an embodiment is envisaged wherein the hydrolysis mixture is filtered, followed by the addition of water or liquid followed by an additional step of extracting the aqueous liquid, e.g. using a chamber filter press, and combining the extracts obtained in the respective cycles. This step may be repeated as many times as desired in order to achieve e.g. a higher yield. The extracted liquid (or combined extract liquids) will typically contain the monosaccharides, including arabinose, pecto-oligosaccharides, pectin (fragments), hemicelluloses (fragments) and mineral acids and salts. The fraction containing the solids may be used as a source of other valuable components.

[0082] The invention also entails embodiments wherein the extracted liquid is used to treat an additional quantity of fresh plant material. This has the advantage that the amount of mineral acid relative to arabinose in the resulting extract is effectively reduced. In some embodiments, the amount of mineral acid relative to arabinose in the produced extract can effectively be reduced by as much as 50 %. Hence, in an embodiment a method as defined herein is provided comprising the steps of: a3) extracting liquid from the mixture obtained in step a2) by solid-liquid separation; a3') intro-

ducing the extracted liquid in a reactor together with a further quantity of the plant material provided in step a1), preferably under agitation and/or heating, optionally in combination with an additional quantity of an aqueous mineral solution; and a3") extracting liquid from the mixture obtained in step a3') by solid-liquid separation.

[0083] It will be understood by those of average skill in the art that the techniques, equipment and conditions employed in step a3') will typically (but not necessarily) be the same as for step a2). Similarly, in step a3") the same techniques will typically be employed as what has been described here above for step a3).

[0084] Embodiments are also envisaged wherein the method comprises two or even more cycles of steps a3) - a3").

[0085] Further described herein is an enriched or purified arabinose fraction obtainable by the method as defined herein.

[0086] Further described is a crysalline arabinose material having a melting point within the range of 155-163 °C and comprising more than 99 % (w/w) arabinose, preferably more than 99.5 % (w/w) more than 99.6 % (w/w), more than 99.7 % (w/w), more than 99.8 % (w/w), or more than 99.9 % (w/w), which is further typically characterized by the presence of detectable amounts of at least one component, at least two components, at least three components, at least four components or at least five components selected from the group consisting of galactose, xylose, rhamnose, glucose, disaccharides, trisaccharides and oligosaccharides.

[0087] Further, a crystalline arabinose material as defined herein is provided, characterized in that it comprises 0.01-0.5 % (w/w) of galactose, e.g. 0.02-0.1 % (w/w); and/or 0.005-0.06 % (w/w) of xylose, e.g. 0.01-0.05 % (w/w). The crystalline arabinose material obtainable by the method of the present invention may further contain residual amounts of water, e.g. amounts up to 1.0 or 0.5 % (w/w).

[0088] The invention has been described by reference to certain embodiments discussed above. It will be recognized that these embodiments are susceptible to various modifications and alternative forms well known to those of skill in the art.

[0089] Accordingly, although specific embodiments have been described, these are examples only and are not limiting upon the scope of the invention.

[0090] Furthermore, for a proper understanding of this document and in its claims, it is to be understood that the verb "to comprise" and its conjugations is used in its nonlimiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

[0091] The following examples are offered for illustrative purposes only, and are not intended to limit the scope of the present invention in any way.

Examples

Example 1: Extraction of sugar beet pulp

[0092] 155 kg of (ensilaged) sugar beet pulp is washed 5 times in a flotation washer to remove sand, clay, rocks, etc. A quantity of 230 kg of washed pulp is obtained (13.14 % dry solids).

[0093] In a stirred tank 220 kg of wahsed pulp and 220 kg water are introduced. Nitric acid is added in a quantity of 1,4 wt.% (HNO_3 relative to total weight). The temperature is increased to and kept at 80°C. Extraction is continued for three hours with continuous stirring.

[0094] The acidic pulp slurry is pumped to a filter press (pump pressure of 0.6 bar overpressure).

Analysis of the acid extract:

Brix	4.83%
Arabinose	1.22%
Pectin	1.85%
Nitrate	1.1%

Example 2: Ultrafiltration of the acid pulp extract

[0095] The acid extract as produced in example 1 is subjected to ultrafiltration. The membrane elements are ceramic with a MWCO of 15 kDa, with a tbular membrane configuration (Tami, France; hydraulic diameter Dh = 3.5 mm; tubular length L = 1178 mm) in multichannel mode (23 chanels). The total membrane surface is 4.9 m^2. The filtration process is performed at a temperature of 40-60°C and a transmembrane pressure (TMP) of 4-5 bar. An amount of 206 kg of the extract is treated and concentrated to a concentration factor CF=1.5. Subsequently the concetrated retentate is dialysed with demi water to a ratio Water: Retentate=3.26. The dialysis is performed at a constant retentate volume. The permeate

flux varied from J=25 lmh to J=20 lmh during concentration and gradually decreased during dialysis to J=15 lmh. The amount of permeate was 494 kg and had a brix value of 1.4% The amount of retentate was 115 kg with a brix value of 3.2%

Analysis:

UF permeate 15 KD		UF retentate 15 KD	
Brix value	1.26%	Brix value	2.82%
Arabinose	0.50%	Arabinose	0.06%
Pectin	0.06%	Pectin	1.97%
Nitrate	4500 ppm	Nitrate	520 ppm

Example 3: nanofiltration of Ultrafiltration 15KD permeate

[0096] The UF 15 KD permeate as produced in example 2 is subjected to nanofiltration. installation. The membrane elements are ceramic and have a MWCO of 1 kDa. The membrane configuration is tubular (Tami, France; hydraulic diameter Dh = 3 .5; tubular length L = 1178 mm) in multichannel mode (23 chanels). The total membrane surface is 2.45 m^2. The filtration process is performed at a temperature of 40-60°C and a transmembrane pressure TMP=4-6 bar. In total 494 kg UF 15KD permeate was treated and concentrated to a concentration factor CF=9.4. No dialysis of the retentate was performed. The permeate flux was J=401 lmh and gradually decreased to 20 lmh at the end of the treatment. Permeate was produced in an amount of 464 kg, which had a brix value of 1.3%. Retentate was produced in an amount of 50kg, which had a Brix value of 2.82%

Analysis:

UF permeate 1 KD		UF retentate 1 KD	
Brixwaaarde	1.36%	Brixwaaarde	2.82%
Arabinose	0.58%	Arabinose	0.72%
Pectin	0%	Pectin	0.02%
Nitrate	4800 ppm	Nitrate	5100 ppm
Unknown	0.09% (oligo)*	Unknown	1.31%(oligo)*
*: the amount or oligosaccharide cannot be determined analytically, as the oligo s are highly reistant to (enzymatic) hydrolysis.			

Example 4: Cation exchange treatment of the UF 1 KD permeate

[0097] Cation exchange treatment is performed in order to exchange the cation in the NF 1 KD permeate, as produced in example 3, against H^+ ions. A macroporous strong acid ion exchange resin is applied; type Lewatit S 1462 (Bayer). The resin is treated with HCl to become fully loaded with H^+. In a batch wise fashion, the permeate of the NF(IKD) is passed over a column packed with the cation exchange resin (2 bed volume an hour). The column height is approximately 1 meter. The temperature is 20-25°C. As total amount of 464 kg permeate UF 1 KD is passed over the column. Am amount of 486 kg eluate is collected.

Analysis:

	permeate 1 KD	eluate
Brix value	1.36%	1.17% (dilution by startingt up and washing off)
Calcium	390 ppm	1 ppm
Potassium	14 ppm	<10 ppm
Magnesium	53 ppm	<1 ppm
Sodium	14 ppm	14 ppm
Arabinose	0.58%	0.48%

Example 5: Nanofiltration (180 Da) of cation exchange eluate

[0098] A nanofiltration treatment is performed to enrich the cation exchange eluate as produced in example 4 in arabinose. An organic membrane element is used having a MWCO of 180 Da. The membrane configuration is spiral wound with a spacer of 46 mill (milliinches). The cartridge length L=40 inch and the diameter D=2.5 inch (Type AMS 3012, AMS, Tel-Aviv, Israel). The membrane surface is 1.6 m^2. The filtration process is performed at a temperature of 20-25°C en a transmembrane pressure (TMP)= 35-40 bar. The process involves a batch-wise concentration of the retentate by withdrawal of the permeate and subsequent dialysis of the retentate (at a constant retentate volume). A concentration factor (CF)=20 is used. The dialysis was done by diluting the retentate with a factor 3 (with demiwater). The permeate flux (J) depended on the arabinose concentration and CF; on average J=30-20 lmh during concentration to CF=20. During the dialysis to W/R=3, J gradually decreases to 20-15 lmh. The retentate comprises arabinose wit traces of oligosaccharides and anions of the extraction acid. The purity of the de arabinose fraction is 68.6%.

Analysis

	Cation ion exchange eluate (before NF)	NF retentate
Brix value%	1.05	11.13
Arabinose%	0.49	7.64
Pectin %	0.06	0.82
Calcium ppm	2.3	34
Potassium ppm	97	1200
Magnesium ppm	0.81	11
Sodium ppm	<10	40
Nitrate%	4300	4000
Purity Arabinose%	42.6	68.6
% NO_3 relative to arabinose	87.7	5.32

Example 6: arabinose crystallization

[0099] Arabinose is crystallized from the NF retentate as produced in example 5. The retentate is concentrated by evaporation to create a state of supersaturation so that cooling crystallization van be performed resulting in the formation of arabinose crystals that can be collected. The mother liquor of the first crystallization is again concentrated to a state of supersaturation and subjected to cooling, thereby forming another quantity of arabinose crystals which are also collected. The combined crystllization yield was 62% of the arabinose originally present. The purity of the crystalls formed in the first crystallization was 99.2%; the purity of the crystalls formed in the second crystallization was 97.8%.

Example 7: Polishing of the NF retentate

[0100] Several polishing steps are performed with the aim of further increasing the purity of the arabinose from the retentate as produced in example 5, thereby increasing the yield in the crystallization process as described in the previous example. The polishing treatment comprises:

- treatment with an anion exchange resin
- sugar fermentation
- active carbon treatment

treatment with anion exchange resin

[0101] The anion exchange treatment is performed to exchange the anions in the NF 180D retentate as produced in example 5, with OH^- ions. A macroporous medium base resin is used (Lewatit S 4268, Bayer). The resin is loaded with OH^- using NaOH. In a batch-wise fashion, the NF 180D retentate is passed over a packed column of the resin, at a rate of 2 bed volumes per hour (BV/h.) The column height was approximately 1 meter. The temperature was kept at 20-25°C. The eluate contains the initial content of sugars. The purity of the arabinose fraction increases from 69% (in the nano-

filtration retentate) to 91.3% in the eluate.

Sugar fermentation

[0102] The sugar fermentation is performed in order to convert the fermentable sugars still present in the arabinose fraction into other byproducts resulting in enhancement of the yield of the crystallization

[0103] To the eluate obtained after anion exchange treatment, baker's yeast (Fermipan Brown, AB Mauri (UK) Ltd) is added at a dose of 2% relative to the dry solids in the eluate, after the pH value has been adjusted to 4.5 ± 0.2 and the temperature has been set to 30°C ± 3°C. The fermentation is allowed to continue for 48 hours, while maintaining the temperature at 30°C and under constant stirring. Thereafter the liquid is separated from solid biomass.

Active carbon treatment

[0104] Active carbon treatment is performed in order to remova color, flavor and/or taste imparting components. To the liquid obtained by fermentation, active carbon powder (type CN1, Norit) is added at a level of 2 gram/l. The mixture is kept at ambient temperature and is continuously stirred for one hour. Subsequently, the active carbon is separated from the liquid by microfiltration using ceramic membrane elements (Tami-Frankrijk) with a pore diameter of 0.2 micrometer in a tubular configuration (hydraulic diameter Dh=3.5 mm; tubular length L=1178 mm) in multichannel mode (23 chanels).

Claims

1. Method of enriching an arabinose fraction containing, besides arabinose, at least one mineral acid, preferably at least one mineral acid selected from the group of nitric acid, hydrochloric acid, sulfuric acid and phosphoric acid, as well as at least one metal cation containing compound, preferably at least one alkali metal or earth alkali metal cation containing compound;
said method comprising the consecutive steps of:

    a) providing an aqueous liquid comprising said arabinose fraction;
    b) subjecting the aqueous liquid to a treatment resulting in the replacement of metal cations by protons, preferably to a treatment selected from cation exchange treatment and electrodialysis;
    c) passing the aqueous liquid obtained in step b) through a nano filtration membrane having a molecular weight cut-off value within the range of 150-250 Da;
    d) collecting the retentate as the enriched arabinose fraction.

2. Method according to claim 1, wherein step b) comprises:

    b1) contacting the aqueous liquid with a protonated cation exchange resin;
    b2) separating the aqueous liquid from the cation exchange resin.

3. Method according to claim 1, wherein the arabinose fraction has a combined level of oligosaccharides and polysaccharides of below 60 % (w/w), based on total dry weight of the arabinose fraction.

4. Method according to claim 1, wherein the arabinose fraction is pre-treated by passing an aqueous liquid comprising said arabinose fraction through a nanofiltration or tight ultrafiltration membrane having a molecular weight cut-off value within the range of 500-5000 Da and collecting the permeate.

5. Method according to claim 4, wherein the arabinose fraction is pre-treated by passing an aqueous liquid comprising said arabinose fraction through an ultrafiltration membrane having a molecular weight cut-off value within the range of 10 - 100 KDa, prior to pre-treatment with the nano filtration- or tight ultrafiltration membrane, and collecting the permeate.

6. Method according to claim 1, wherein the arabinose fraction is produced by a process comprising the consecutive steps of:

    a1) providing an arabinose containing plant material, preferably a plant pulp, more preferably a spent sugar beet pulp;

a2) placing the plant material in a reactor with an aqueous mineral acid solution, preferably under agitation and/or heating;
a3) extracting liquid from the reactor by solid-liquid separation;
a4) treating the extracted liquid by passing it through an ultrafiltration membrane having a molecular weight cut-off value within the range of 10 - 100K Da and collecting the permeate; and
a5) treating the permeate by passing it through a nanofiltration - or tight ultrafiltration membrane having a molecular weight cut-off value within the range of 500 - 5000 Da and collecting the permeate.

7. Method according to claim 6, wherein step a2) comprises placing the plant material in a reactor with an aqueous solution of a mineral acid, preferably an aqueous solution of nitric acid, hydrochloric acid, sulfuric acid or phosphoric acid, more preferably an aqueous solution comprising nitric acid at a concentration of 1-3 % (w/v).

8. Method according to any one of claims 6 or 7, wherein step a2) comprises placing the spent plant material in a reactor with an aqueous mineral acid solution and heating the solution to a temperature within the range of 50 - 100 °C, for a period of time within the range of 60 - 240 minutes, preferably under agitation.

9. Method according to any one of claims 6-8, wherein step a3) comprises extracting liquid from the reactor and subjecting it to a solid-liquid separation process, preferably macrofiltration, centrifuging and/or decantation.

10. Method according to any one of claims 1-9, wherein step b) is performed using a strong acid cation exchange resin (SAC).

11. Method according to any one of claims 1-10, wherein step c) is performed using a nanofiltration membrane having a molecular weight cut-off value within the range of 170-200 Da.

12. Method according to claim 11, wherein the nanofiltration membrane is selected from the group consisting of acid stable organic membranes.

13. Method according to any one of the preceding claims, said method further comprising the steps of:
e) subjecting the retentate obtained in step d) to one or more polishing treatments, preferably to one or more polishing treatments selected form (i) Anion exchange treatment; (ii) fermentative treatment; and (iii) active carbon treatment.

14. Method of producing crystalline arabinose, said method comprising the steps a)-d) or a)-e), as defined in any one of claims 1-13, said method further comprising the step of:
f) inducing crystallization of arabinose from the retentate obtained in step d) or the polished retentate obtained in step e).

Patentansprüche

1. Verfahren zum Anreichern einer Arabinosefraktion enthaltend, neben Arabinose, zumindest eine Mineralsäure, bevorzugt zumindest eine Mineralsäure ausgewählt aus der Gruppe von Salpetersäure, Salzsäure, Schwefelsäure und Phosphorsäure, sowie zumindest eine Metallkationenenthaltende Verbindung, bevorzugt zumindest eine Alkalimetall- oder Erdalkalimetallkationen-enthaltende Verbindung;
das Verfahren umfassend die aufeinanderfolgenden Schritte von:

a) Bereitstellen einer die Arabinosefraktion umfassenden wässrigen Flüssigkeit;
b) Unterwerfen der wässrigen Flüssigkeit einer Behandlung resultierend in dem Ersatz von Metallkationen durch Protonen, bevorzugt einer Behandlung ausgewählt aus Kationenaustauschbehandlung und Elektrodialyse;
c) Durchleiten der in Schritt b) erhaltenen wässrigen Flüssigkeit durch eine Nanofiltrationsmembran mit einem Molekulargewichtsgrenzwert innerhalb des Bereichs von 150-250 Da;
d) Sammeln des Retentats als die angereicherte Arabinosefraktion.

2. Verfahren nach Anspruch 1, wobei Schritt b) umfasst:

b1) Kontaktieren der wässrigen Flüssigkeit mit einem protonierten Kationenaustauschharz;
b2) Trennen der wässrigen Flüssigkeit von dem Kationenaustauschharz.

3. Verfahren nach Anspruch 1, wobei die Arabinosefraktion einen kombinierten Gehalt von Oligosacchariden und Polysacchariden basierend auf dem Gesamttrockengewicht der Arabinosefraktion von unter 60% (w/w) aufweist.

4. Verfahren nach Anspruch 1, wobei die Arabinosefraktion vorbehandelt wird durch Hindurchleiten einer die Arabinosefraktion umfassenden wässrigen Flüssigkeit durch eine Nanofiltrations- oder dichte Ultrafiltrationsmembran mit einem Molekulargewichtsgrenzwert innerhalb des Bereichs von 500-5000 Da und Sammeln des Permeats.

5. Verfahren nach Anspruch 4, wobei die Arabinosefraktion vorbehandelt wird durch Hindurchleiten einer die Arabinosefraktion umfassenden wässrigen Flüssigkeit durch eine Ultrafiltrationsmembran mit einem Molekulargewichtsgrenzwert innerhalb des Bereichs von 10-100 KDa,
vor der Vorbehandlung mit der Nanofiltrations- oder dichten Ultrafiltrationsmembran, und Sammeln des Permeats.

6. Verfahren nach Anspruch 1, wobei die Arabinosefraktion hergestellt ist durch einen Prozess umfassend die aufeinanderfolgenden Schritte von:

a1) Bereitstellen eines Arabinose-enthaltenden Pflanzenmaterials, bevorzugt einer Pflanzenpulpe, mehr bevorzugt verbrauchte Zuckerrübenpulpe;
a2) Platzieren des Pflanzenmaterials in einem Reaktor mit einer wässrigen Mineralsäurelösung, bevorzugt unter Rühren und/oder Erwärmen;
a3) Extrahieren von Flüssigkeit von dem Reaktor durch Fest-Flüssig-Trennung;
a4) Behandeln der extrahierten Flüssigkeit durch Hindurchleiten durch eine Ultrafiltrationsmembran mit einem Molekulargewichtsgrenzwert innerhalb des Bereichs von 10-100 KDa und Sammeln des Permeats; und
a5) Behandeln des Permeats durch Hindurchleiten durch eine Nanofiltrations- oder dichte Ultrafiltrationsmembran mit einem Molekulargewichtsgrenzwert innerhalb des Bereichs von 5-5000 Da und Sammeln des Permeats.

7. Verfahren nach Anspruch 6, wobei Schritt a2) umfasst Platzieren des Pflanzenmaterials in einem Reaktor mit einer wässrigen Lösung einer Mineralsäure, bevorzugt einer wässrigen Lösung von Salpetersäure, Salzsäure, Schwefelsäure oder Phosphorsäure, mehr bevorzugt einer wässrigen Lösung umfassend Salpetersäure bei einer Konzentration von 1-3% (w/v).

8. Verfahren nach einem der Ansprüche 6 oder 7, wobei Schritt a2) umfasst Platzieren des verbrauchten Pflanzenmaterials in einem Reaktor mit einer wässrigen Mineralsäurelösung und Erwärmen der Lösung auf eine Temperatur innerhalb des Bereichs von 50-100°C, für eine Zeitspanne innerhalb des Bereichs von 60-240 Minuten, bevorzugt unter Rühren.

9. Verfahren nach einem der Ansprüche 6 bis 8, wobei Schritt a3) umfasst
Extrahieren von Flüssigkeit aus dem Reaktor und Unterwerfen desselben einem Fest-Flüssig-Trennprozess, bevorzugt Makrofiltration, Zentrifugieren und/oder Dekantieren.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei Schritt b) unter Verwendung eines starken Säurekationenaustauschharzes (SRC) durchgeführt wird.

11. Verfahren nach einem der Ansprüche 1 bis 10, wobei Schritt c) unter Verwendung einer Nanofiltrationsmembran mit einem Molekulargewichtsgrenzwert innerhalb des Bereichs von 170-200 Da durchgeführt wird.

12. Verfahren nach Anspruch 11, wobei die Nanofiltrationsmembran ausgewählt ist aus der Gruppe bestehend aus säurestabilen organischen Membranen.

13. Verfahren nach einem der vorstehenden Ansprüche, das Verfahren ferner umfassend die Schritte:
e) Unterwerfen des in Schritt d) erhaltenen Retentats einer oder mehr Polierbehandlungen, bevorzugt ein oder mehr Polierbehandlungen ausgewählt aus (i) Anionenaustauschbehandlung; (ii) fermentativer Behandlung; und (iii) Aktivkohlebehandlung.

14. Verfahren zum Herstellen von kristalliner Arabinose, das Verfahren umfassend die Schritte a) bis d) oder a) bis e), wie in einem der Ansprüche 1 bis 13 definiert, das Verfahren ferner umfassend den Schritt von:
f) Induzieren der Kristallisation von Arabinose aus dem in Schritt d) erhaltenen Retentat oder dem in Schritt e) erhaltenen polierten Retentat.

Revendications

1. Procédé d'enrichissement d'une fraction d'arabinose contenant, outre de l'arabinose, au moins un acide minéral, de préférence au moins un acide minéral choisi dans le groupe de l'acide nitrique, l'acide chlorhydrique, l'acide sulfurique et l'acide phosphorique, ainsi qu'au moins un composé contenant des cations métalliques, de préférence au moins un composé contenant des cations de métal alcalin ou de métal alcalino-terreux ;
ledit procédé comprenant les étapes consécutives suivantes :

   a) fournir un liquide aqueux comprenant ladite fraction d'arabinose ;
   b) soumettre le liquide aqueux à un traitement entraînant le remplacement des cations métalliques par des protons, de préférence à un traitement choisi parmi un traitement d'échange de cations et une électrodialyse ;
   c) faire passer le liquide aqueux obtenu à l'étape b) à travers une membrane de nanofiltration présentant une valeur limite de poids moléculaire comprise entre 150 et 250 Da ;
   d) recueillir le rétentat en tant que fraction d'arabinose enrichie.

2. Procédé selon la revendication 1, dans lequel l'étape b) comprend :

   b1) la mise en contact du liquide aqueux avec une résine échangeuse de cations protonée ;
   b2) la séparation du liquide aqueux d'avec la résine échangeuse de cations.

3. Procédé selon la revendication 1, dans lequel la fraction d'arabinose présente un niveau combiné d'oligosaccharides et de polysaccharides inférieur à 60 % en poids par rapport au poids sec total de la fraction d'arabinose.

4. Procédé selon la revendication 1, dans lequel on prétraite la fraction d'arabinose en faisant passer un liquide aqueux comprenant ladite fraction d'arabinose à travers une membrane de nanofiltration ou d'ultrafiltration serrée présentant une valeur limite de poids moléculaire comprise entre 500 et 5 000 Da et en recueillant le perméat.

5. Procédé selon la revendication 4, dans lequel on prétraite la fraction d'arabinose en faisant passer un liquide aqueux comprenant ladite fraction d'arabinose à travers une membrane d'ultrafiltration présentant une valeur limite de poids moléculaire comprise entre 10 et 100 kDa, avant le prétraitement par la membrane de nanofiltration ou d'ultrafiltration serrée, et en recueillant le perméat.

6. Procédé selon la revendication 1, dans lequel la fraction d'arabinose est produite par un processus comprenant les étapes consécutives suivantes :

   a1) fournir une matière végétale contenant de l'arabinose, de préférence une pulpe végétale, plus préférablement un résidu de pulpe de betterave sucrière ;
   a2) placer la matière végétale dans un réacteur avec une solution acide minérale aqueuse, de préférence sous agitation et/ou chauffage ;
   a3) extraire le liquide du réacteur par séparation solide-liquide ;
   a4) traiter le liquide extrait en le faisant passer à travers une membrane d'ultrafiltration présentant une valeur limite de poids moléculaire comprise entre 10 et 100 kDa et recueillir le perméat ; et
   a5) traiter le perméat en le faisant passer à travers une membrane de nanofiltration ou d'ultrafiltration serrée présentant une valeur limite de poids moléculaire comprise entre 500 et 5 000 Da et recueillir le perméat.

7. Procédé selon la revendication 6, dans lequel l'étape a2) comprend le placement de la matière végétale dans un réacteur avec une solution aqueuse d'un acide minéral, de préférence une solution aqueuse d'acide nitrique, d'acide chlorhydrique, d'acide sulfurique ou d'acide phosphorique, plus préférablement une solution aqueuse comprenant de l'acide nitrique à une concentration comprise entre 1 et 3 % en poids par rapport au volume.

8. Procédé selon l'une quelconque des revendications 6 ou 7, dans lequel l'étape a2) comprend le placement du résidu de matière végétale dans un réacteur avec une solution aqueuse d'un acide minéral et le chauffage de la solution à une température comprise entre 50 et 100°C, pendant une durée comprise entre 60 et 240 minutes, de préférence sous agitation.

9. Procédé selon l'une quelconque des revendications 6 à 8, dans lequel l'étape a3) comprend l'extraction de liquide du réacteur et l'application d'un processus de séparation solide-liquide à celui-ci, de préférence par macrofiltration, centrifugation et/ou décantation.

10. procédé selon l'une quelconque des revendications 1 à 9, dans lequel on effectue l'étape b) en utilisant une résine échangeuse de cations fortement acide (SAC).

11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel on effectue l'étape c) en utilisant une membrane de nanofiltration présentant une valeur limite de poids moléculaire comprise entre 170 et 200 Da.

12. Procédé selon la revendication 11, dans lequel la membrane de nanofiltration est choisie dans le groupe constitué des membranes organiques stables en milieu acide.

13. Procédé selon l'une quelconque des revendications précédentes, ledit procédé comprenant en outre les étapes suivantes :
c) soumettre le rétentat obtenu à l'étape d) à un ou plusieurs traitements de polissage, de préférence à un ou plusieurs traitements de polissage choisis parmi (i) un traitement d'échange d'anions ; (ii) un traitement de fermentation ; et (iii) un traitement par du charbon actif

14. Procédé de production d'arabinose cristalline, ledit procédé comprenant les étapes a) à d) ou a) à e), telles que définies à l'une quelconque des revendications 1 à 13, ledit procédé comprenant en outre l'étape suivantes :
f) induire la cristallisation d'arabinose à partir du rétentat obtenu à l'étape d) ou du rétentat poli obtenu à l'étape e).

REFERENCES CITED IN THE DESCRIPTION

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