Abstract:
The invention relates to an improved process for producing plant stanol by hydrogenating plant sterol in an organic solvent at a hydrogen pressure of 1-200 bar in the presence of a hydrogenation catalyst.
Improved hydrogenation process

Plant sterols are compounds appearing in plant material and they are commercially isolated from edible oil refining residues or from crude tall oil, which is a wood pulping by-product stream. The plant sterols consist typically of several individual compounds; campesterol, sitosterol, stigmasterol and sitostanol being the most common chemical structures.

The plant sterol production process from edible oil refining residues ("deodoriser distillates, DOD") consists typically of the following steps:

1. esterification of free acids and liberation of sterols from sterol esters
2. optional evaporation of the light fractions to remain the sterols in the residue
3. optional evaporation of the free sterol fraction
4. crystallisation of free sterols from a sterol rich fraction obtained from step 1, 2 or 3, and
5. optional recrystallisation of the sterols to make the pure sterol product.

In the optional recrystallisation process mentioned above the used crystallisation solvents are typically aliphatic hydrocarbons wherein some lower alcohol (methanol or ethanol) and water has been added. Alternatively ethanol as such can be used.

In plant sterol production from wood pulping by-product streams the actual raw material is tall oil pitch ("TOP"). Tall oil pitch is the distillation residue from the tall oil refining process which produces fatty acids and resin acids for the chemical industry. Tall oil is the acidulated product of organic extractives recovered from cooking liquor ("black liquor") produced in the wood pulping process.

The sterol extraction process from tall oil pitch typically consists of
1. liberation of sterols from sterol esters by saponification
2. optional acidulation or neutralisation of free acids present
3. evaporation of the light fraction from the dried saponificated mixture from step 1 or from the acidulated or neutralised mixture from step 2 to remain the sterols in the residue
4. evaporation of the residue of step 3 to obtain a sterol rich fraction
5. crystallisation of the sterols from the sterol rich fraction, and
6. optional recrystallisation of the sterols to make the pure sterol product.

The crystallisation and/or the optional recrystallisation solvent in the process of isolating sterols from TOP is typically an aliphatic hydrocarbon or a mixture of aliphatic hydrocarbons wherein some water and lower alcohol (methanol or ethanol) is added or a ketone based solvent (typically a mixture of methyl ethyl ketone, lower alcohol and water).
During recent years plant sterol based compounds have become common as cholesterol lowering ingredients in so called functional foods. In these applications the plant sterol based compounds are added into food products e.g. spreads and yoghurts in free form or esterified with fatty acids, typically derived from vegetable oils. In one preferred mode of application these sterols are prior to addition into foods or prior to esterification saturated by catalytic hydrogenation to produce plant stanols. Plant stanols are thus compounds in which no double bonds found in the original sterol structure can be found due to hydrogen addition into the double bonds of the sterol molecule. The advantages of stanols over sterols include e.g. better stability against oxidation and lower absorbability into the blood circulation from the digestive tract, which have been shown to be highly desirable properties.

The commercial production of stanols has taken place in a separate process using isolated and purified sterols as the substrate in the hydrogenation process. Typically these commercial stanol production processes use precious metal (e.g. palladium) as catalyst and the reaction medium is n-propanol or isopropanol.

It has now been realized that from the manufacturing point of view it would be advantageous to hydrogenate the sterols to stanols in the connection of the sterol isolation process whereby the number of overall process unit operations can be minimized. This makes it possible to maximize the stanol yield in this process design. This invention deals with such an integrated process and is based on the findings that stanol containing residues from the stanol crystallisation are possible to recirculate into the sterol isolation process and recover the stanol in the sterol crystallisation stage without negative effects on the sterol isolation processes. Hence, the recovery of the expensive plant stanol from residue streams is technically possible with minimum amount of additional steps and investments.

Also purification of sterols to high purity required for the hydrogenation process is feasible in this process. Therefore, optionally, into this integrated sterol isolation and hydrogenation process also removal of trace impurities, which may interfere with the hydrogenation process, by adsorbent and/or absorbent treatment can preferably be included.

Moreover, the solvent compositions used in the sterol purification can be used at least partly as hydrogenation and subsequent stanol crystallisation solvents instead of currently used propanol, which does not work properly in the sterol purification.

**Detailed description of the invention**
The essential content of the invention is recirculation of stanol residues from the mother liquor of the stanol purification crystallisation to the sterol rich fraction from which sterol purification crystallisation take place. Optional trace impurity removal processes by absorbent and/or adsorbent treatment are preferably performed in the stage where purified sterol material is dissolved in a solvent before hydrogenation. Further benefits are achieved by conducting the hydrogenation of sterol to stanol in at least partly and preferably essentially the same solvent composition that is used in sterol purification crystallisation in the sterol isolation process. When stanol is produced in a production unit integrated with sterol isolation and purification, no separate solvent recycling equipments are needed for the hydrogenation solvent recycling. By this procedure also the necessity of the final steps of sterol production - drying and packaging - and thereby a considerable amount of investment costs are avoided. Thus, the process according to the invention comprises the following steps:

a. Providing a sterol rich fraction for sterol purification crystallisation by any known method. This can be done by first liberating sterols from sterol esters by e.g. saponification, then concentrating the sterols e.g. by distillation, extraction and/or crystallisation. Examples of preparations of sterol rich fractions are disclosed e.g. in US 2704764 (example 1), US 6815551 (examples 4, 6 and 7), WO 2008/099051 and FI 20080174.

b. Dissolving the sterol rich fraction into a solvent by heating. The solvent preferably comprises at least one organic solvent and optionally water. The organic solvent may be alkanol (e.g. methanol, ethanol or propanol), hydrocarbon (e.g. heptane) or ketone (e.g. methyl ethyl ketone or methyl isobutyl ketone). The solvent can be e.g. ethanol as such or mixed with propanol or methanol ; mixture of ketone, alkanol and water ; or mixture of hydrocarbon, alkanol and water. Thus it is preferable to use at most three solvents of which two are organic solvents and one is water.

c. Crystallising the sterol by cooling and isolating the sterol cake by filtration.

d. Optionally dissolving and recrystallising the sterol from stage c using a solvent and/or washing the sterol from stage c with a solvent. The solvent preferably comprises at least one organic solvent and optionally water. More preferably, the solvent comprises at least one same organic component with the solvent of step b. Even more preferably, the solvents used in steps b and d comprise the same components, i.e. essentially the same solvent is used in both steps. The components may also exist in about same weight ratio.

e. Dissolving the sterol from purification steps c or d into a solvent. Also this solvent preferably comprises at least one organic solvent and optionally water. More preferably, the solvent comprises at least one same organic component with the solvent of step b. Even more preferably, the solvents used in steps b and e comprise the same components, i.e.
essentially the same solvent is used in both steps. The components may also exist in about same weight ratio.

f. Optionally treating the dissolved sterol by adsorbent and/or absorbent material. This will remove trace impurities which might interfere with hydrogenation by lowering the activity of the catalyst i.e. poisoning the catalyst. This is accomplished in an absorbent and/or adsorbent bed or by mixing the solution with the absorbent and/or adsorbent material and removing the absorbent and/or adsorbent e.g. by filtration. Suitable absorbents and/or adsorbents are e.g. activated carbon, bleaching earth, spent hydrogenation catalyst, and other precious metal catalysts than Pd (e.g. Ni). A Pd-catalyst that has been used for hydrogenation of sterols (here called a spent catalyst) can be used again in pre-purification although the activity for use in hydrogenation would be too low. The spent catalyst used for pre-purification can be removed before performing the hydrogenation with new catalyst. It is also convenient to leave the spent catalyst used in pre-purification in the hydrogenation reaction mixture and only add active Pd-catalyst to the mixture to perform the hydrogenation. During the hydrogenation the impurities will remain attached to the spent catalyst used in the pre-purification and will not hamper the hydrogenation reaction. The removal of catalyst can then be made more easily by removing both catalyst used in the pre-purification and catalyst used for hydrogenation at the same time. The use of other precious metal catalysts e.g. nickel for pre-purification is effective. Before adding the Pd-catalyst for hydrogenation the Ni-catalyst has to be removed in order not to mix the catalyst, but make the reuse and regeneration of them possible.

g. Hydrogenating the sterols dissolved in solvent from step e or f to stands at suitable hydrogenation conditions. The hydrogen pressure may vary from 1-200 bar, and the lower range of the temperature is chosen so that the sterol is completely dissolved and at most it may be 200 °C. The sterol content in the solvent can be from 5 % to 50 % by weight, h. Removing catalyst. This is preferably done by filtration

i. Crystallising stands from the hydrogenated mixture. This can be accomplished by cooling and/or partially evaporating the solvent,

j. Separating the stanol crystals preferably by filtration and optionally washing the crystals with a solvent. The solvent preferably comprises at least one organic solvent and optionally water. More preferably, the solvent comprises at least one same organic component with the solvent of step b. Even more preferably, the solvents used in steps band j comprise the same components, i.e. essentially the same solvent is used in both steps. The components may also exist in about same weight ratio. The filtrate and optionally the optionally used washing solvent form a mixture called mother liquor.

k. Adding at least part of the crystallisation residue remaining in the mother liquor of step j to any proceeding step in the isolation or purification process of sterols. Preferred steps are step b or d. The mother liquid of step j can be added essentially as such or in partially or
totally dried form which is obtained by recovering at least part of the solvent from the mother liquor of step j. By this recirculation step of the stanol a more complete recovery of stanols in the total process is obtained. Thus at least part of the mother liquor is recirculated as such or in concentrated form. The dry matter of the mother liquor may also be washed before recirculation. Preferably 5-100 %, more preferably 50-100 % and even more preferably 80-100 % of the crystallisation residue is added in step k.

By the expression "essentially the same solvent" is here meant that the solvent used in one step consists of the same components, e.g. at least one organic solvent and optionally water, in comparison to the solvent used in another step but the weight ratio of the components may vary. Preferably, also the weight ratios are the same or almost the same. The solvent may also consist only of one component, e.g. one organic solvent, and is then of course the same in both steps.

It has now been realized that suitable solvents in the hydrogenation reaction of plant sterols to plant stanols are (all % given are by weight):
- lower alkanol,
preferrably ethanol, a mixture of ethanol (80-99.5 %) and methanol (0.5-20 %), or a mixture of ethanol (80-99.5 %) and propanol (0.5-20 %),
- a mixture of hydrocarbon, alkanol and water,
preferrably a mixture of hydrocarbon (2-98 %), alkanol (2-98 %) and water (0.1-5 %), more preferably a mixture of hydrocarbon (70-97 %), alkanol (2-28 %) and water (1-10 %), and most preferably a mixture of hydrocarbon (85-90 %), alkanol (5-10 %) and water (1-5 %). Preferably the hydrocarbon is a C5-C12 aliphatic or acyclic hydrocarbon, or a mixture of such hydrocarbons, more preferably it is heptane. Preferably the alkanol is a C1-C3 alkanol, more preferably methanol or ethanol, and most preferably methanol.
- a mixture of ketone, alkanol and water,
preferrably a mixture of ketone (50-80 %), alkanol (10-40 %) and water (3-15 %), more preferably a mixture of ketone (60-80 %), alkanol (15-35 %) and water (7-12 %), still more preferably a mixture of ketone (50-80 %), alkanol (10-40 %) and water (3-15 %), and most preferably a mixture of ketone (60-80 %), alkanol (15-35 %) and water (7-12 %). Preferably the ketone is methyl ethyl ketone ("MEK") or methyl isobutyl ketone ("MiBK"), more preferably MEK. Preferably the alkanol is methanol or ethanol, more preferably methanol.

It has also been realized that the above mentioned solvent compositions can be used through the whole process of crystallising sterols, hydrogenating them to stanols and crystallising the stanols.
When using mixtures of hydrocarbon, alkanol and water as solvent in certain solvent ratios (when alkanol and especially water contents are increased e.g. when evaporating hydrocarbon), the separation of phases will take place at some conditions. In the hydrogenation processes it is also possible to perform the hydrogenation reaction in such a solvent, which has separated into two phases. The reaction will then occur in the upper (hydrocarbon) phase of the solvent mixture. In practice this may be useful and simpler than mixing the solvent components in correct ratios for the solvent mixture to remain in one phase during the hydrogenation.

Solvents are easily recycled in a useful way by using common evaporation and distillation systems. E.g. the used solvent from steps b-d is combined with the used solvent from step e-f, impurities are removed by evaporation or distillation before or after the combination, the components or at least the organic solvents are separated and reused in solvents of the process steps. In certain solvent systems it is possible to take advantage of phase separation instead or in addition to the separation of individual components. E.g. when the solvent comprises hydrocarbon (heptane), alkanol (methanol or ethanol) and water, it is possible to have upper phase rich in hydrocarbon to be directed to the hydrogenation step and lower phase rich in alkanol and water to be directed to the sterol isolation and purification steps.

Example 1
Preparing plant stanol from DOD

1.1. Producing a sterol rich fraction (step a)
25 parts by weight of soy deodoriser distillate from soy bean oil refining and a solution of 12.9 parts sulphuric acid in 400 parts of methanol were refluxed for 8 hours. The mixture was cooled to 10 °C. The precipitate was filtered, washed with methanol and air dried in vacuum. The yield was 13 % of the distillate. This sterol rich fraction contained 89 % by weight sterols.

1.2. Crystallisation and washing of sterols (steps b-d)
Crystallisation was performed by dissolving at refluxing temperature the sterol rich fraction in ethanol (1 part sterol rich fraction and 10 part ethanol) and then cooling to 18 °C recrystallisation temperature. The crystals were filtered by using vacuum and washed with fresh solvent. The mass yield in the crystallisation was 78 % by weight of sterol cake (calculated as dry) and the sterol purity was 95.5 % by weight. No stanols were present.

1.3. Hydrogenation without pre-purification (steps e, g)
50 g (by dry weight) of the sterol cake obtained in the process above (solids content 70 %) was slurried in 450 g ethanol. The mixture was transferred into a 1 liter pressure reactor and flushed three times with nitrogen. 10 g of a mixture containing 0.5 g Pd/C catalyst (palladium dispersed on charcoal support material, 5 % Pd content) in ethanol was then added into the reactor through a feeding funnel. The system was pressurized with hydrogen twice and closed gas tight. To the system a hydrogen stream was led so that the pressure increased to 4.0 bars. The reactor included good mixing. The mixture was heated to a temperature of 100 °C. After 30, 60, 90 and 120 minutes reaction time samples of the reaction mixture were taken and the conversion rate was measured by GC analysis.

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Unreacted sterols, % *</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>37.6</td>
</tr>
<tr>
<td>60 min</td>
<td>19.7</td>
</tr>
<tr>
<td>90 min</td>
<td>9.9</td>
</tr>
<tr>
<td>120 min</td>
<td>4.9</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

1.4. Hydrogenation after pre-purification with activated carbon (steps e-g)

50 g of the sterol cake (the same as in the example above) was slurried into 450 g ethanol.

1.5 g of activated carbon (Norit SXIG) was added and the solution was mixed for 0.5 hours at reflux temperature. The carbon was separated from the hot mixture by filtration. Thereafter the reaction mixture was transferred into a pressure vessel and hydrogenated as above. The amount of unreacted sterols developed as follows:

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Unreacted sterols, % *</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>18.3</td>
</tr>
<tr>
<td>60 min</td>
<td>3.4</td>
</tr>
<tr>
<td>90 min</td>
<td>1.5</td>
</tr>
<tr>
<td>120 min</td>
<td>1.4</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

1.5. Recovery of sterols/stanols from the crystallisation residue (steps h-j)

The catalyst was filtered from the hot reaction mixture after the hydrogenation reaction by using pressure filtration. After this the stanol product was crystallised by cooling the mixture to 18 °C. The Stanol crystals were filtrated and washed with fresh ethanol. The mass yield in the crystallisation was 82 % while 18 % of the mass remained in the mother liquor. The crystals contained 68 % stanols.
1.6. Recirculation (step k)
Most of the ethanol from the mother liquor from above was evaporated and the residue was
recirculated into the sterol recovery process (step b-d) as follows:
Into 50 g of crude sterols (from step a) and H g of the solid residue obtained from the
mother liquor above 550 g fresh ethanol was added. The mixture was heated to reflux
temperature so that all the solid material was dissolved and thereafter it was cooled to 18
°C. The sterol cake was filtrated and washed with fresh ethanol. The mass of the dried cake
was 50.5 g (83 % mass yield) and the sterol content (including stanols) was 96 %. The
stanol content in the crystallised product was 3.4 % meaning that 90 % of the total stanols
were recovered. The reason to the better yield of stanols in relation to sterols in this
recovery process is the slightly smaller solubility in ethanol of stanols compared to sterols.

**Example 2**
Preparing plant stanol from Scandinavian tall oil pitch

2.1. Producing a sterol rich fraction (step a)
Scandinavian tall oil pitch was used as raw material. The pitch was saponified with NaOH-
solution, the saponified pitch was then dried by thin film evaporation and the sterol rich
fraction was isolated by short path evaporation from the mixture. The sterol rich fraction
contained 30.4 % desmethylsterols and considerable amount of methyl and
dimethylsterols.

2.2. Crystallisation and washing of sterols (steps b-d)
The isolation of sterols was performed by crystallisation as follows:
1 part of the sterol rich fraction was dissolved into 3 parts of solvent mixture in a pressure
vessel at 100 °C temperature. The solvent mixture consisted of 65 % methylethylketone,
25 % methanol and 10 % water. After dissolution the mixture was cooled to 20 °C and the
sterol was filtered and washed thoroughly with fresh crystallisation solvent.
The isolated sterol product (purity 93.5 %) was recrystallised from a solvent mixture
consisting of 65 % methylethylketone, 25 % methanol and 10 % water. Solids to solvent
ratio was 1:10 and crystallisation temperature 20 °C. The sterol content (including stanols)
of the cake was 98.5 % by dry weight. The stanol content of the cake was 10.5 % by dry
weight (stanols naturally occurring in the sterol mixture from wood).

2.3. Hydrogenation without pre-purification (steps e, g)
Hydrogenation was performed according to Example 1.3 but in a solvent mixture
consisting of 65 % by weight methylethylketone, 25 % by weight methanol and 10 % by
weight water. Thus, the wet (solids content 70 %) cake was slurried into the solvent
mixture and the measures as in Example 1.3 were accomplished. The amount of unreacted sterols developed as follows:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Unreacted sterols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>42.0</td>
</tr>
<tr>
<td>60</td>
<td>28.6</td>
</tr>
<tr>
<td>90</td>
<td>20.0</td>
</tr>
<tr>
<td>120</td>
<td>14.4</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

2.4. Hydrogenation after pre-purification with activated carbon (steps e-g)

50 g of the sterol cake (the same as in Example 2.3) was slurried into 450 g of a solvent mixture consisting of 65 % methylethylketone, 25 % methanol and 10 % water. 1.5 g of activated carbon (Norit SXIG) was added and the solution was mixed for 30 min at reflux temperature. The carbon was separated from the hot mixture by filtration. Thereafter the reaction mixture was transferred into a pressure vessel and hydrogenated as above. The amount of the unreacted sterols developed as follows:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Unreacted sterols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>27.6</td>
</tr>
<tr>
<td>60</td>
<td>11.5</td>
</tr>
<tr>
<td>90</td>
<td>5.0</td>
</tr>
<tr>
<td>120</td>
<td>3.1</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

2.5. Hydrogenation after pre-purification with carbon and bleaching clay (steps e-g)

Pre-purification and hydrogenation were performed according to example 2.4, except that in addition to 1.5 g activated carbon also 1.0 g bleaching clay (Tonsil Optimum FF) was added. The amount of the unreacted sterols after hydrogenation developed as follows:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Unreacted sterols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>19.8</td>
</tr>
<tr>
<td>60</td>
<td>9.7</td>
</tr>
<tr>
<td>90</td>
<td>2.7</td>
</tr>
<tr>
<td>120</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

2.6. Recovery of sterols and stands from the crystallisation residue (steps h-j)
The catalyst was filtrated from the hot reaction mixture obtained from Example 2.4 after the hydrogenation reaction by using pressure filtration. After this the stanol product was crystallised by cooling the mixture to 20 °C. The stanol crystals were filtered and washed with a fresh solvent mixture of MEK, MeOH and water (65:25:10 by weight). The mass yield was 80 % while 20 % of the mass remained in the mother liquor. The crystals contained 65 % stanols.

2.7. Recirculation (step k)
Most of the solvent mixture from the mother liquor above was evaporated and this residue was recirculated into the sterol crystallisation phase (step b-d) as follows:

Into 50 g sterol rich fraction (from Example 2.1) and H g of solid from the mother liquor above 550 g fresh solvent mixture (MEK, MeOH and water; ratios as above) was added. The mixture was heated to reflux temperature so that all the solid material was dissolved and thereafter cooled to 20 °C. The sterol cake was filtrated and washed with fresh solvent mixture. The mass of the dried cake was 49.5 g (81 % mass yield) and sterols content (including stanols) was 98.5 %. The stanol content in the crystallised product was 22.5 % indicating that most of the stanols from the mother liquor were recovered.

Example 3
Preparing plant stanol from US tall oil pitch

3.1. Producing a sterol rich fraction (step a)
The sterol rich fraction was produced as in Example 2.1 by using short path distillation from dried saponified tall oil pitch. The desmethylsterol content was 42.3 % (higher sterol content than in Example 2 due to different raw material quality; the amount of methyl and dimethyl sterols was negligible compared to Example 2).

3.2. Crystallisation and washing of the sterols (steps b-d)
500 g of the sterol rich fraction from Example 3.1 was mixed with 1500 g of solvent mixture, which consisted of heptane (88 % by weight), methanol (9 % by weight) and water (3 % by weight). The mixture was heated and mixed until all the solids were dissolved and thereafter cooled to 20 °C. The crystallised sterols were filtered and washed with fresh solvent of the same composition as used in the crystallisation. The purity of recovered sterols was 97 % (measured from dried sample).

3.3. Hydrogenation of sterols without pre-purification (steps e, g)
The hydrogenation was accomplished as in Example of 1.3. However, in this case the solvent used had the same composition as the solvent mixture used in the sterol crystallisation phase of this example. The reaction proceeded as follows:
Unreacted sterols, %

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Unreacted sterols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>47.0</td>
</tr>
<tr>
<td>60 min</td>
<td>30.1</td>
</tr>
<tr>
<td>90 min</td>
<td>24.5</td>
</tr>
<tr>
<td>120 min</td>
<td>16.1</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

3.4. Hydrogenation of sterols after pre-purification with spent catalyst (steps e-g)

50 g of the moist sterol cake (dry weight) was slurried into 450 g fresh crystallisation solvent of the same composition as in Example 3.2. 0.5 g of spent catalyst that had been washed in 10 ml of a heptane/methanol solvent mixture was added and the solution was mixed for 30 min at reflux temperature. The catalyst was separated from the hot mixture by filtration. Thereafter the reaction mixture was transferred into a pressure vessel and new catalyst was added. Hydrogenation in the solvent of this example was performed at conditions defined in Example 1.3. The amount of the unreacted sterols developed as follows:

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Unreacted sterols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>25.4</td>
</tr>
<tr>
<td>60 min</td>
<td>8.7</td>
</tr>
<tr>
<td>90 min</td>
<td>4.5</td>
</tr>
<tr>
<td>120 min</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

3.5. Hydrogenation of sterols after pre-purification with Nickel-catalyst (steps e-g)

The procedure of Example 3.4 was repeated except that the spent catalyst was replaced by new Nickel catalyst (Raney Nickel, 0.04 g catalyst calculated as Ni-metal). The amount of the unreacted sterols developed as follows:

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Unreacted sterols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>23.4</td>
</tr>
<tr>
<td>60 min</td>
<td>7.9</td>
</tr>
<tr>
<td>90 min</td>
<td>4.1</td>
</tr>
<tr>
<td>120 min</td>
<td>2.0</td>
</tr>
</tbody>
</table>

* percentage of free sterols of the dry weight of the reaction mixture sample from which the catalyst had been removed by filtration

3.6. Recovery of sterols and stanols from the crystallisation residue (steps h-j)
The catalyst was filtrated using pressure filtration from the hot reaction mixture (from Example 3.4) after the hydrogenation reaction had stopped. After this the stanol product was crystallised by cooling the mixture to 20 °C. The stanol crystals were filtered and washed with fresh solvent mixture (heptane, methanol and water; ratio by weight 88:9:3). The mass yield was 77% while 23% of the mass remained in the mother liquor. The crystals contained 67% stanols.

3.7. Recirculation of stanols (step k)

Most of the solvent mixture from the mother liquor from Example 3.6 was evaporated and the residue was recirculated into the sterol crystallisation phase (3.2; step b) as follows:

Into 50 g crude sterols (from 3.1) and H g of the solid from the mother liquor above 550 g fresh solvent mixture (composition as in Example 3.1) was added. The mixture was heated to the reflux temperature so that all the solid material was dissolved and thereafter it was cooled to 20 °C. The sterol cake was filtrated and washed with a fresh solvent mixture (composition as in Example 3.1). The mass of the dried cake was 48.5 g (79.5% mass yield) and the sterols content (including stanols) was 98.5%. The stanol content in the crystallised product was 22.0% indicating that most of the stanols from the mother liquor were recovered.

The invention relates to a process for preparing plant sterol comprising the following steps:

a. providing a sterol rich fraction for sterol purification crystallisation by any known method,
b. dissolving the sterol rich fraction into a solvent by heating,
c. crystallising the sterol by cooling and isolating the sterol cake by filtration,
d. optionally dissolving and recrystallising and/or washing the sterol from stage c using a solvent,
e. dissolving the sterol from purification steps c or d into a solvent,
f. optionally treating the dissolved sterol by adsorbent and/or absorbent material,
g. hydrogenating the dissolved sterol to stanols at suitable hydrogenation conditions using a catalyst,
h. removing the catalyst,
i. crystallising stanol from the hydrogenated mixture,
j. separating the stanol crystals preferably by filtration and optionally washing the crystals with a solvent characterised in that
k. adding at least part of the crystallisation residue remaining in the mother liquor of step j to any proceeding step (b-d) in the isolation and purification process of the sterol, preferably to step b or d and more preferably to step b.
In the process preferably 5-100 %, more preferably 50-100 % and even more preferably 80-100 % of the crystallisation residue remaining in the mother liquor is added to any proceeding step, preferably to step b, in the isolation and purification of the sterol.

In the process preferably the solvents used in steps b-j comprise at least one organic solvent and optionally water.

In the process preferably the solvents used in steps b-j comprise at least one organic solvent selected from the group of alkanol, hydrocarbon and ketone.

In the process preferably the solvents used in steps b-j comprise at least one same organic solvent.

In the process preferably at most three solvents are used in steps b-j.

In the process preferably the solvents used in steps b-j comprise the same organic solvents and the optional water.

In the process preferably the solvents used in steps b-j are essentially the same.

In the process preferably the solvent used in any one of steps b-j comprise at least one lower alkanol, preferably ethanol, more preferably a mixture of ethanol (80-99.5 % by weight) and propanol (0.5-20 % by weight), and most preferably a mixture of ethanol (80-99.5 % by weight) and methanol (0.5-20 % by weight).

In the process preferably the solvent used in any one of steps b-j comprise a mixture of ketone, alkanol and water, more preferably a mixture of ketone (50-80 % by weight), alkanol (10-40 % by weight) and water (3-15 % by weight), even more preferably a mixture of ketone (60-80 % by weight), alkanol (15-35 % by weight) and water (7-12 % by weight), still more preferably a mixture of ketone (50-80 % by weight), alkanol (10-40 % by weight) and water (3-15 % by weight), and most preferably a mixture of ketone (60-80 % by weight), alkanol (15-35 % by weight) and water (7-12 % by weight). The ketone is preferably MEK or MiBK, more preferably MEK. The alkanol is preferably C1-C3 alkanol, more preferably methanol or ethanol and even more preferably methanol.

In the process preferably the solvent used in any one of steps b-j comprise a mixture of hydrocarbon, alkanol and water, more preferably hydrocarbon (2-98 % by weight), alkanol (2-98 % by weight) and water, even more preferably a mixture of hydrocarbon (70-97 %
by weight), alkanol (2-28 % by weight) and water (1-10 % by weight), and most preferably a mixture of hydrocarbon (85-90 % by weight), alkanol (5-10 % by weight) and water (1-5 % by weight). The hydrocarbon is preferably at least one C5-C12 aliphatic or acyclic hydrocarbon, more preferably heptane. The alkanol is preferably a C1-C3 alkanol, more preferably methanol or ethanol, even more preferably methanol.
Claims

1. A process for preparing plant stanol comprising the following steps:
   a. providing a sterol rich fraction for sterol purification crystallisation by any known method,
   b. dissolving the sterol rich fraction into a solvent by heating,
   c. crystallising the sterol by cooling and isolating the sterol cake by filtration,
   d. optionally dissolving and recrystallising and/or washing the sterol from stage c using a solvent,
   e. dissolving the sterol from purification steps c or d into a solvent,
   f. optionally treating the dissolved sterol by adsorbent and/or absorbent material,
   g. hydrogenating the dissolved sterol to stanols at suitable hydrogenation conditions using a catalyst,
   h. removing the catalyst,
   i. crystallising stanol from the hydrogenated mixture,
   j. separating the stanol crystals preferably by filtration and optionally washing the crystals with a solvent characterised in that
   k. adding at least part of the crystallisation residue remaining in the mother liquor of step j to any proceeding step (b-d) in the isolation and purification process of the sterol,
   l. preferably to step b or d and more preferably to step b.

2. The process according to claim 1 characterised in that 5-100 %, preferably 50-100 % and more preferably 80-100 % of the crystallisation residue is added in step k.

3. The process according to claim 1 or 2 characterised in that the solvents used in steps b-j comprise at least one organic solvent and optionally water.

4. The process according to claim 1 or 2 characterised in that the solvents used in steps b-j comprise at least one organic solvent selected from the group of alkanol, hydrocarbon and ketone.

5. The process according to claims 1-4 characterised in that the solvents used in steps b-j comprise at least one same organic solvent.

6. Process according to any one of claims 1-5 characterised in that at most three solvents are used in steps b-j.
7. The process according to any one of claims 1-6 characterised in that the solvents used in steps b-j comprise the same organic solvents and the optional water.

8. The process according to any one of claims 1-7 characterised in that the solvents used in steps b-j are essentially the same.

9. The process according to any one of claims 1-8 characterised in that the solvent used in any one of steps b-j comprise at least one lower alkanol, preferably ethanol, more preferably a mixture of ethanol (80-99.5 % by weight) and propanol (0.5-20 % by weight), and most preferably a mixture of ethanol (80-99.5 % by weight) and methanol (0.5-20 % by weight).

10. The process according to any one of claims 1-8 characterised in that the solvent used in any one of steps b-j comprise a mixture of ketone, alkanol and water, preferably a mixture of ketone (50-80 % by weight), alkanol (10-40 % by weight) and water (3-15 % by weight), more preferably a mixture of ketone (60-80 % by weight), alkanol (15-35 % by weight) and water (7-12 % by weight), still more preferably a mixture of ketone (50-80 % by weight), alkanol (10-40 % by weight) and water (3-15 % by weight), and most preferably a mixture of ketone (60-80 % by weight), alkanol (15-35 % by weight) and water (7-12 % by weight).

11. The process according to claim 10 characterised in that the ketone is MEK or MiBK, preferably MEK.

12. The process according to claim 10 or 11 characterised in that the alkanol is C1-C3 alkanol, preferably methanol or ethanol and more preferably methanol.

13. The process according to any one of claims 1-8 characterised in that the solvent used in any one of steps b-j comprise a mixture of hydrocarbon, alkanol and water, preferably hydrocarbon (2-98 % by weight), alkanol (2-98 % by weight) and water (0.1-5 % by weight), more preferably a mixture of hydrocarbon (70-97 % by weight), alkanol (2-28 % by weight) and water (1-10 % by weight), and even more preferably a mixture of hydrocarbon (85-90 % by weight), alkanol (5-10 % by weight) and water (1-5 % by weight).

14. The process according to claim 13 characterised in that the hydrocarbon is at least one C5-C12 aliphatic or acyclic hydrocarbon, preferably heptane.
15. The process according to claim 13 or 14 characterised in that alkanol is a C1-C3 alkanol, preferably methanol or ethanol, more preferably methanol.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C07J, C11B

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

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Epo-Internal, WPI, Medline, Biosis, XPESP, COMPDX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search
22 October 2009 (22.10.2009)

Date of mailing of the international search report
06 November 2009 (06.11.2009)

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