(54) Title: EXTRACTION OF AMYGDALIN FROM FRUIT KERNELS

(57) Abstract

A method of producing a foodstuff from fruit kernels comprising deskinning the kernels, subsequently debittering the kernels by extraction with water, processing the debittered kernels to the final foodstuff, and recovering amygldalin from the extract formed by the debittering of the kernels.
| AM | Armenia | GB | United Kingdom | MW | Malawi |
| AT | Austria | GE | Georgia | MX | Mexico |
| AU | Australia | GN | Guinea | NE | Niger |
| BB | Barbados | GR | Greece | NL | Netherlands |
| BE | Belgium | HU | Hungary | NO | Norway |
| BF | Burkina Faso | IE | Ireland | NZ | New Zealand |
| BG | Bulgaria | IT | Italy | PL | Poland |
| BJ | Benin | JP | Japan | PT | Portugal |
| BR | Brazil | KE | Kenya | RO | Romania |
| BY | Belarus | KG | Kyrgyzstan | RU | Russian Federation |
| CA | Canada | KP | Democratic People's Republic of Korea | SD | Sudan |
| CF | Central African Republic | KR | Republic of Korea | SE | Sweden |
| CG | Congo | KZ | Kazakhstan | SG | Singapore |
| CH | Switzerland | LI | Liechtenstein | SI | Slovenia |
| CI | Côte d'Ivoire | LK | Sri Lanka | SK | Slovakia |
| CM | Cameroon | LR | Liberia | SN | Senegal |
| CN | China | LT | Lithuania | SZ | Swaziland |
| CS | Czechoslovakia | LU | Luxembourg | TD | Chad |
| CZ | Czech Republic | LV | Latvia | TG | Togo |
| DE | Germany | MC | Monaco | TJ | Tajikistan |
| DK | Denmark | MD | Republic of Moldova | TT | Trinidad and Tobago |
| EE | Estonia | MG | Madagascar | UA | Ukraine |
| ES | Spain | ML | Mali | UG | Uganda |
| FI | Finland | MN | Mongolia | US | United States of America |
| FR | France | MR | Mauritania | UZ | Uzbekistan |
| GA | Gabon | | | VN | Viet Nam |
Extraction of amygdalin from fruit kernels

The present invention relates to a method of producing a foodstuff, such as marzipan and perzipan, from fruit kernels, such as almond kernels and apricot kernels, comprising deskinning the kernels, subsequently debittering the kernels by extraction with water and processing the debittered kernels to the final foodstuff.

It is known to produce amygdalin from apricot kernels by extraction of comminuted kernels with hot benzine. After the extraction the kernel residue is inapplicable both for direct use and as starting material for further processing into e.g. marzipan.

Marzipan is produced from i.a. almond kernels and apricot kernels. In the production of marzipan an extraction of the kernels is effected in order to extract the bitter substances, such as amygdalin, which give the kernels an undesired bitter taste.

In a prior art method of producing marzipan standing of the extract causes amygdalin to be cleaved due to the action of enzymes also present in the extract. The cleavage is effected according to the following reaction scheme:

Amygdalin + H₂O → Prunasin + C₆H₁₂O₆

Prunasin → C₆H₅HOHCN + C₆H₁₂O₆

C₆H₅HOHCN → C₆H₅CHO + HCN

The enzymes work optimally at a pH value of 4.5 and a temperature of about 55°C, but a certain decomposition of amygdalin into benzaldehyde and hydrogen cyanide will also occur at room temperature and higher pH values.

In the prior art method it may be necessary to remove the
toxic cyanide formed before the extract can be discharged to the environment.

The object of the present invention is to provide an improved method of the type stated in the introductory part of claim 1.

This object is obtained with the method according to the invention, which is characterized in that amygdalin is recovered from the extract formed by the debittering of the kernels.

The invention is based on the discovery that the extract contains a large amount of amygdalin which has not hitherto been used but merely been allowed to undergo enzymatic decomposition, and that it is possible to recover this amount of amygdalin provided that it is done immediately after the extraction of the kernels is completed, i.e. before any significant decomposition of amygdalin occurs.

The method according to the invention has the further advantage that only an insignificant amount of cyanide will be formed in the extract, and as a result thereof the separation of the cyanide from the extract, which process is laborious and costly, can be completely avoided.

The kernels used for the method according to the invention are preferably almond kernels, apricot kernels, plum seeds, cherry seeds, peach stones and mixtures thereof, preferably a mixture of almond kernels and apricot kernels. The raw kernels typically have a water content of about 5% by weight.

Amygdalin, also called vitamin B17, has the following chemical formula: C_{20}H_{27}NO_{11}. Amygdalin is used i.a. as a medicament for the treatment of cancer. Apricot kernels and bitter almond kernels have a content of amygdalin of about 3-4% by weight.
When a mixture of two or several types of fruit kernels is used, each type of kernel is preferably deskinned and debittered separately.

The kernels are deskinned by boiling and blanching.

Initially the raw kernels are subjected to boiling (blanching) in order to loosen the skins of the kernels. The boiling is usually effected by charging the kernels into a water bath having a temperature of e.g. about 98°C for a short period of e.g. 2-4 minutes. The boiling may e.g. be effected in a continuously working boiler in the form of a bended pipe having two oblique parallel pipe legs with open ends, said boiler being provided with an endless cable to which blade plates are attached by which the kernels fed through a funnel at the bending of the pipe are conveyed through the pipe containing the heated water bath.

After boiling the kernels typically have a water content of about 12% by weight.

After boiling the boiled kernels are blanched, i.e. the loosened skins are separated from the rest of the kernels. The blanching may e.g. be effected by conveying the kernels through one or more consecutive sets of rollers, wherein the rollers of the individual pair of rollers rotate oppositely at different velocity.

The deskinned kernels are then subjected to a debittering process by which amygdalin is extracted from the kernels with water. The extraction is preferably effected in two consecutive steps which e.g. may be carried out in vessels provided with agitators.

The extraction can be effected at a temperature of about 5-30°C.

In the first extraction step a water amount of from 2 to 4
parts by weight per part by weight of kernels on a wet basis is used, preferably about 3 parts by weight of water per part by weight of kernels on a wet basis. The first extraction step preferably takes about 12-30 hours.

After completion of the first extraction step, the kernels and the water phase containing the extracted amygdalin, i.e. the extract, are separated. The separation can be effected by filtration, e.g. with a macrofilter located in the bottom of the extraction vessel.

In the second extraction step a water amount of from 3 to 10 parts by weight per part by weight of kernels on a wet basis may be used, preferably about 7 parts by weight of water per part by weight of kernels on a wet basis. The second extraction step preferably takes about 12-36 hours.

In both extraction steps the kernels have a water content of about 40-50% by weight.

A purification of amygdalin from the extract formed in the extraction is then effected. For this purpose only the extract from the first extraction step is ordinarily used, whereas the extract from the second extraction step, which has a relatively small content of amygdalin, is ordinarily discarded.

The purification of amygdalin from the extract is preferably initiated immediately after the completion of the extraction and the separation of kernels and extract in order to minimize the conversion of amygdalin into benzaldehyde and hydrogen cyanide and glucose.

In the purification of amygdalin from the extract, a concentration of the extract is optionally effected initially. The concentration is preferably effected by reverse osmosis, whereby membranes of the thin film composite membrane type e.g. may be used.
In order to optimize the concentration of amygdalin it is preferred to use soft water as the use of hard water may cause precipitation of various compounds, such as calcium carbonate, when the corresponding ions are concentrated by the reverse osmosis, and as the precipitated compounds will deposit on the membrane and cause it to clot, thereby causing a reduction in the effectiveness of the membrane.

Therefore, soft water is preferably used for the first extraction step.

Reverse osmosis may result in a concentration of amygdalin of up to about 10 times.

The purification of amygdalin from the optionally concentrated aqueous extract is preferably effected by liquid/liquid extraction using an extraction agent.

As extraction agent benzine, ether, hexan, toluene and other solvents which are non-miscible with water can be used.

The liquid/liquid extraction is preferably effected at elevated temperature.

In the liquid/liquid extraction amygdalin is drawn over into the extraction agent phase, and the extraction agent phase and the aqueous phase are then separated by e.g. sedimentation.

The separated extraction agent phase is then evaporated by heating to crystallize the amygdalin.

The liquid/liquid extraction is preferably carried out in a column apparatus, preferably a fully automatic column apparatus with recirculation of the SOXLET type.

The crystallized amygdalin is finally purified to yield
crystalline amygdalin having a purity of up to 99%.

The purification is effected in a number of steps, each step comprising a) redissolution of the crystals in a suitable solvent, such as benzine, ether, hexan, toluene and other solvents which are non-miscible with water, b) evaporation to recrystallization, and c) filtration of the evaporation residue. The purification of the crystals is continued until the desired purity is obtained and ordinarily comprises between 3 and 10 steps.

The purification of the crystals is preferably carried out in a column apparatus, preferably a fully automatic column apparatus with recirculation of the SOXLET type.

The liquid/liquid extraction and the subsequent purification can be carried out in an integrated apparatus.

Prior to the further processing of the debittered kernels an organoleptic assessment of the kernels is carried out in order to decide whether a sufficient debittering has been obtained.

Subsequently the debittered kernels are processed to the final foodstuffs to be produced.

The final processing of the debittered kernels into marzipan/perzipan will be described in further detail below.

In the final processing a separation of water from the second extraction step is initially effected, which separation can be carried out in a press or a centrifuge. After pressing the kernels typically have a water content of about 28-32% by weight.

The kernels are then mixed with cane sugar and glucose and other optional ingredients, such as sorbitol, in an
appropriate mixing ratio. The resulting mixture is then grinded. The grinding may e.g. be effected with rollers of stone or with a stator/rotor of steel, such as a stator/rotor of the Stephan Microput brand.

The grinded mixture is finally roasted to form a final mass having a water content of from about 12 to about 17% by weight.

Example

1 Ton of apricot kernels having a water content of about 5% by weight was boiled in a pipe-formed continuously working boiler at a temperature of about 98°C and a retention time of 4 minutes.

The skins of the kernels were then removed in an apparatus consisting of four consecutive pairs of rollers, wherein the two rollers of each pair of rollers rotate oppositely and wherein one roller of each pair of rollers rotates at the double speed of that of the cooperating roller.

The deskinning was followed by a separation of any foreign bodies, such as stones, and of kernels which had not been deskinned or only partially deskinned. The separation consisted in two steps, viz. firstly an automatic separation using photo cells and then a manual visual separation.

The deskinned kernels were then charged into a vessel having a quadratic cross-section and a centrally located stirrer, and 3 m³ of soft water was added. The mixture of kernels and water was then stirred in the vessel for a period of 24 hours at a temperature of 20°C.

The water phase was then separated from the kernels by filtration through a macrofilter located in the bottom of the vessel. The separated water phase had an amygdalin content of about 0.4% by weight.
The water phase was then concentrated about 10 times by reverse osmosis using a thin film composite membrane.

The concentrated water phase having a volume of about 300 l was subsequently extracted with 2 x 20 l of benzine in a column apparatus, and the benzine phase was then separated from the water phase by sedimentation in a sedimentation tank.

The separated benzine phase was placed in a heated steel tank and evaporated in vacuo at a temperature of about 80°C. The evaporation residue was then filtered and rinsed with benzine to yield about 12 kg of crystalline amygdalin on a dry basis.

The raw crystals obtained were redissolved in benzine, evaporated in vacuo, filtered and rinsed with benzine. This treatment was repeated for a total of 6 times, yielding crystalline amygdalin having a purity of about 99%.
CLAIMS

1. A method of producing a foodstuff from fruit kernels comprising deskinning the kernels, subsequently debittering the kernels by extraction with water, and processing the debittered kernels to the final food stuff, characterized in that amygdalin is recovered from the extract formed by the debittering of the kernels.

2. A method according to claim 1, characterized in that the extraction is effected in two consecutive steps, and that amygdalin is recovered from the extract from the first extraction step.

3. A method according to claim 1 or 2, characterized in that a concentration of the extract is effected.

4. A method according to claim 3, characterized in that the concentration is effected by reverse osmosis.

5. A method according to claim 4, characterized in that soft water is used for the extraction.

6. A method according to any of the preceding claims, characterized in that a purification of amygdalin from the extract is effected by liquid/liquid extraction with an extraction agent.

7. A method according to claim 6, characterized in that benzine is used as extraction agent.

8. A method according to claim 6 or 7, characterized in that the extraction agent phase is separated from the aqueous phase and evaporated to crystallize the amygdalin.
9. A method according to claim 8, characterized in that the crystals are purified in a number of steps, each step comprising a) redissolution of the crystals in a suitable solvent, b) evaporation to recrystallization, and c) filtration of the evaporation residue.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

**IPCG**: A61K 31/70, A23L 1/211  
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)

**IPCG**: A61K, A23L

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

SE,DK,F1,N0 classes as above

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

**DIALINDEX(FOODSCI), WPI, CLAIMS/US PATENTS, JAPIO, EPODOC**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>Acta Chemica Scandinavica B, Volume 32, 1978, Godtfriedsen, S.E. et al., &quot;Bitterness in Aqueous Extracts of Apricot Kernels&quot; page 588 - page 592</td>
<td>1,3,6,7</td>
</tr>
<tr>
<td>X</td>
<td>Dialog Information Service, File 351, WPI, Dialog accession no. 010031986, WPI accession no. 94-299699/37, (KUMAI M), &quot;Use of crude drug essence compsn. contg. nitrile glycoside - having anticaner activity&quot;, &amp; JP 6 227 998 A, publ. (940816)</td>
<td>1</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

---

Date of the actual completion of the international search: **22 March 1996**  
Date of mailing of the international search report: **02-04-1996**  
Authorized officer: **INGA-KARIN PETERSSON**  
Telephone No.: **+46 8 782 25 00**
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

---

A

Dialog Information Service, File 51, FSTA, Dialog accession no. 00092653, FSTA accession no. 75-02-j0272, Salem, S.A.: "Egyptian peach kernel seeds", Deutsche Lebensmittel-Rundschau, 1974, 70 (10) 359-360

---

---