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METHOD OF PREPARING VALUABLE MATERIALS WITH THE AID OF INVERTEBRATES

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This invention pertains to new products of dietary value and processes for their production. More particularly, it refers to products resulting from the controlled fermentation of invertebrate organisms.

Heretofore invertebrata have been found to contain large amounts of provitamin D. In particular, it was found that mussels had a surprisingly high content of provitamin D. U. S. Patent No. 2,163,659, issued June 27, 1939, on an application filed by Boer, van Niekerk, Reerink and van Wijk, discloses and claims this important contribution to the art.

When provitamin D is extracted from mussels and other invertebrata a large amount of residue is obtained as a practically worthless by-product. This residue comprises the flesh of the mussel or other invertebrata, substantially free from provitamin D. It contains large quantities of albumen and has a surprisingly high nutritive value. Due to its unpleasant smell and the presence of indigestible constituents, however, it is of little practical value, particularly insofar as its use for human consumption is concerned.

It is an object of this invention to prepare new dietary products of excellent nutritive value. A further object is to convert mussels and other invertebrata to palatable and readily digested foodstuffs. A still further object is to convert by-products from processes for the production of provitamin D to products of value for human consumption. A still further object is to treat invertebrata in such manner that the provitamin D may be obtained therefrom in an efficient manner and a large portion of the non-provitamin D content thereof may be converted to products of considerable dietary value. A still further object is to produce an entirely new class of products suitable for human consumption, possessing in addition to high nutritive values appreciable quantities of the antirachitic factor, vitamin D. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained according to the herein described invention wherein invertebrate organisms are digested under acid conditions for a sufficient period of time to cause partial decomposition of the nitrogen-containing molecules thereof, and thereafter the soluble constituents are separated therefrom. In a more restricted sense this invention is directed to the treatment of invertebrates under controlled conditions in order to effect decomposition of the albumen content thereof and in order to eliminate therefrom those constituents which are indigestible or unpalatable, then separating the liquid portion of the resulting digestion mass, treating it with an alkali and drying under mild conditions. In a more restricted sense this invention is concerned with the digestion of comminuted mussels at slightly elevated temperatures and under moderately acid conditions for a sufficient period of time to substantially decompose the albumen content thereof, heat-sterilizing the resulting digestion mass and separating therefrom the liquid fraction thereof, substantially neutralizing the resulting liquid and reducing its water content under vacuum. In its preferred embodiment this invention pertains to the digestion of comminuted mussels at a temperature of about 37° C. to about 40° C., in an aqueous solution having a pH of about one to about four, for a period of at least one day, heat sterilizing the resulting mass and separating the liquid from the residue thereof, substantially neutralizing the liquid and evaporating it to dryness under reduced pressure.

In carrying out this invention the provitamin D content of the invertebrata may be removed therefrom substantially unimpaired, either before, during or after the aforesaid digestion operation. Furthermore, a portion or all of the provitamin D content of the invertebrata may be permitted to remain therein and may subsequently be antirachitically activated in order to impart antirachitic properties to the resulting products.

The invention may be more readily understood by a consideration of the following illustrative examples:

Example I

Living mussels were shelled and the flesh was comminuted in a hammer mill. The flesh paste contained 78.1% moisture. On a dry basis, this paste contained 9.55% of nitrogen, 1.94% of fat and 0.158% of sterols. To 256 grams of this paste were added 60 cc. of 2 normal hydrochloric acid, producing a solution having a pH between one and two. The mass was then stirred for 60 hours while being maintained at a temperature of between 37° C. and 40° C. Thereafter, it was boiled for a short time with the addition of some water, and filtered.

The undigested matter was washed with a small quantity of water. The clear filtrate was shaken with petroleum ether and neutralized by adding 50 cc. of 2 normal sodium hydroxide. It was then evaporated to dryness in vacuo (bath tempera-

ture 40° C.). After evaporation the dry residue from the filtrate amounted to 39 grams, of which 5.69% was determined to be nitrogen. The nitrogen content of the evaporated residue was, therefore, approximately 41.4% of that contained in the starting material.

The evaporated product had a light brown color and a pleasing briny taste. It could be used in the same manner as a meat extract or cereal.

The undigested residue had a weight of 26 grams and was found to contain 11.97% nitrogen. This indicated that approximately 58% of the nitrogen present in the starting material was contained in this residue. The residue was thoroughly extracted with ethyl alcohol and petroleum ether. 3.70 grams of fatty material was extracted in this manner. Extraction of the filtrate, previously referred to, with petroleum ether produced an additional 0.08 gram of fatty material. The total fat content extracted amounted to 1.48% of the starting material.

From the fatty material extracted as above there were 374 milligrams of sterol or 0.146%, based on the starting material. This amounted to 92% of the total amount of sterol present in the starting material. In consequence of the relatively high acidity of the solution during digestion, the provitamin has suffered appreciable decomposition, 23% only being recovered.

Example 2

310 grams of the same paste referred to in Example 1 has added thereto 30 cc. of 2 normal hydrochloric acid. This produced a solution having a pH of about 4. The mass was then stirred and heated at a temperature between 37° C. and 40° C. for a period of about 12 hours. At the end of this period 5 additional ccs. of 2 normal hydrochloric acid were added in order to reduce the pH, which had increased slightly, to about 4. The digestion was continued at approximately the same temperature for 48 hours, making a total digestion time of about 60 hours.

After filtration it was found that the residue contained 26.8% of the nitrogen present in the starting material, while the filtrate contained approximately 73.2% of the nitrogen from the starting material.

The filtrate was evaporated to dryness under vacuum, producing a product having a brown color and a peptone-like smell and taste. By adding to this a little extract of vegetables a very palatable broth was prepared therefrom.

451 milligrams of sterol were obtained, by the procedure outlined in Example 1, this amounted to 92% of the quantity present in the starting material. The provitamin D content of the sterol was approximately 73% of the provitamin D content of the starting material.

Example 3

228 grams of a mussel paste containing 81.7% moisture and 10.4% nitrogen, on a dry basis, was digested with 27 cc. of 2 normal hydrochloric acid for a period of 63 hours. During the course of this digestion 13 addition ccs. of 2 normal hydrochloric acid was added in order to maintain the pH of the solution at approximately 3. Except for the aforesaid modifications the material was treated in the same manner as referred to in Example 1.

The clear filtrate contained 2.86 grams of nitrogen, amounting to 67% of the nitrogen content of the initial material. The indigestible residue had a weight of 15.6 grams and contained 8.95% of nitrogen, which was 32% of the nitrogen originally present in the mussel paste.

The fatty material was extracted from the undigested residue and the sterol fraction separated therefrom. This sterol fraction amounted to 80% of that present in the starting material and contained 40% of the provitamin originally present.

Example 4

Living shrimp were comminuted, shell and all, in a hammer mill. The paste thus obtained contained 77% of moisture; and had a nitrogen content, on a dry basis, of 10.22%.

1000 grams of this paste were acidulated by adding 100 cc. of 3 normal hydrochloric acid, producing a solution having a pH of about 2. During the addition of acid an intense bubbling and foaming was produced. When the addition of acid was completed the paste was stirred for 24 hours at a temperature of about 37° C. to about 40° C. During this digestion the pH of the solution was maintained at about 2 by adding 2 normal hydrochloric acid from time to time.

When the liquid was separated from the digestion mass it was found that the undigested residue contained 63.8% of the nitrogen present in the starting material. Approximately 36.2% of the nitrogen initially present had been converted to acid soluble product.

Example 5

910 grams of the paste referred to in the preceding example had added thereto 80 cc. of 3 normal hydrochloric acid in order to produce a solution having a pH of about 3. Digestion was carried out for a period of about 24 hours, in the same manner as mentioned in Example 1. It was found that after filtration the filtrate contained 46.7% of the nitrogen present in the starting material.

Example 6

1040 grams of the paste from the preceding example were treated with 65 cc. of 3 normal hydrochloric acid in order to produce a solution having a pH of about 4. Digestion was carried on for a period of about 24 hours, the treatment otherwise being similar to that described in Example 1. After filtration it was found that 62.7% of the nitrogen present in the initial material was present in the filtrate.

In each of the three preceding examples the final foodstuffs had a slightly bitter taste, due to the presence of appreciable amounts of calcium chloride resulting from the action of the acid on the shell of the invertebrata. By means of dialysis through a collodion membrane, with tap water, these taste spoiling constituents could be completely removed. It was found that this dialysis results in the loss of a portion of the nitrogen present in the solution.

Example 7

177 grams of a paste obtained by grinding shelled fresh mussels was centrifuged. The solid matter was stirred with water and centrifuged anew. The liquids collected by the aforesaid centrifuging were extracted a few times with petroleum ether, acidulated with hydrochloric acid to a pH of about 2 and stored. The solid matter was extracted with ethyl alcohol and petroleum ether. The fat extracted thereby was united with the extract from the centrifuging solution. From this fatty fraction the sterol content was separated by well known methods.

The extracted mussel flesh was treated with hydrochloric acid until the solution had a pH of between 1 and 2. It was then stirred for about 24 hours at a temperature maintained at about 37° C. to about 40° C. The digestion mass was subsequently treated in the same manner as described in Example 1.

The filtrate was found to contain 1.08 grams of the nitrogen present in the starting material, which amounted to about 33.3% of this nitrogen. The undigested residue contained about 1.79 grams of the nitrogen present in the initial material, amounting to about 55.1% thereof. Approximately 11% of the nitrogen was lost by this process.

194 milligrams of sterols were obtained, amounting to about 82% of that present in the initial material. No appreciable deterioration or loss of provitamin D had occurred.

It is to be understood that the aforesaid examples are illustrative only of the present invention. They may be varied widely as respects the materials acted upon and the operating conditions, without departing from the scope hereof.

In place of the invertebrata referred to therein other species of invertebrata may be used. Since the various classes and subclasses of invertebrata are well known it is unnecessary to give a detailed description thereof. In particular, it has been found that aquatic invertebrata having a shelled exterior are of optimum value over a wide range of conditions. Among these invertebrata mention may be made of mussels, periwinkles, oysters, whelks, shrimp, and the like. It is understood, of course, that the innumerable species of each of these classes are contemplated for use, as well as mixtures of two or more thereof.

The inverterata should advisably be untainted when used in accordance with this invention. Because of this, ordinary sanitary precautions should be followed in collecting, storing and shipping these invertebrata prior to use herein.

Since these inverterata contain large quantities of valuable provitamin D, as mentioned in U. S. Patent No. 2,163,659, it is contemplated that this constituent may be separated therefrom and that the residue thereof may be converted in part to foodstuffs of high nutritive value and palatability. The provitamin D content of the initial material may be separated from the invertebrata either before, during or after digestion. Separation of provitamin D prior to digestion of the material should advisably be accomplished in such manner that the subsequent digestion operation is not interfered with. For this purpose one should select a process of extracting provitamin D which has no appreciably deleterious effect upon the proteolytic ferment content of the invertebrata.

If one desires, the provitamin D content of the invertebrata may be retained therein or only a portion thereof may be extracted. The residuary provitamin D may then be antirachitically activated in situ. This results in the production of a product having valuable antirachitic properties in addition to excellent palatability and nutritive values. The methods of antirachitic activation are well known and need not be discussed herein. For all practical purposes it may be mentioned that ultra violet irradiation is generally recommended for this activation.

Where the invertebrata are possessed of shells it is generally advisable, although not essential, that the shells be removed before digestion of the organism. Shells may be removed from crustaceans by hand or by one of the many mechanical separation processes. For example, in the case of shrimp and related shell fish, the shells may be removed by utilizing two inclined rollers of rubber arranged in such close proximity to each other that the shell is caused to pass between the rollers and the flesh paste is carried off along an inclined gutter formed by the rollers.

With crustaceans, it is also possible to crush the shells by means of rough crushing tools, without causing the flesh to lose its desirable characteristics. Separation of the pieces of shell and bruised flesh may then be effected, for instance, by hydraulic classification methods.

It is also contemplated that the shelled invertebrata may be ground up, shell and all. This may be accomplished with the aid of a hammer mill or similar apparatus. The flesh paste may then be separated from the ground shell mass by washing, centrifuging, decantation, hydraulic classification, or other well known methods.

When the method of separating the shell from the flesh results in the comminution of this flesh, as in the immediately preceding process, it is advisable to expedite this separation as much as possible. The reason for this is that when the flesh is comminuted fermentation is accelerated, particularly when the hydrogen ion concentration of the mass is in the neighborhood of the neutral point. Since fermentation is only desirable under controlled conditions, this uncontrolled type should be avoided as much as possible for optimum results.

It is also contemplated that the shell may be removed by the addition of large quantities of acids. The expense of this process would, however, be considerable. Likewise, it would generally be necessary to remove the resulting salts before a palatable product could be obtained.

As previously mentioned, the provitamin D may be separated from the residue of the invertebrata either before, during or after the digestion process. This separation is obtained by the use of suitable fat dissolving agents. Where one wishes to isolate the fatty content of the invertebrata prior to digestion this may advantageously be accomplished by repeated extractions with a solvent which does not have a deleterious effect upon the activity of the proteolytic ferments, and which though not miscible with water in all proportions, still has some solubility in water, such as for instance methyl-ethyl-ketone, secondary butyl alcohol, ethyl acetate, diisopropyl ether.

It is also contemplated that the comminuted paste of invertebrata flesh may be dried prior to separation of the provitamin content thereof. This drying may advantageously be accomplished in somewhat the same manner as the preparation of milk powder. The Krause system of preparing milk powder is well adapted thereto. In preparing this dried material care should be taken to select such conditions that neither the proteolytic ferment nor the provitamin D content are damaged during the drying operation. Since these conditions will vary somewhat, depending upon the particular drying operation selected and the particular invertebrata treated, a few simple tests should be sufficient, in any given instance, to determine the best conditions for this purpose.

Another method effecting separation of the provitamin D content without harmfully influencing the resulting dietary product comprises

the centrifuging of the ground fresh flesh of the invertebrata. The centrifuged flesh mass is then dried and its provitamin D content extracted therefrom. The extracted flesh mass is thereafter added to the liquid which had previously been centrifuged therefrom, and the resulting mass digested under such conditions as to produce a valuable dietary product in accordance with the instructions hereof.

Still another feasible method for separating provitamin D from the invertebrata prior to its digestion is to treat the comminuted fresh flesh with ethyl alcohol in order to reduce its water content and thereafter treat the flesh with a fat solvent such as ether, ether containing ethyl alcohol, di-isopropyl ether, di-isopropyl ether containing ethyl alcohol, and the like. After the fatty material is extracted therefrom the fat solvents are removed from the extracted flesh by customary methods, such as vaporization at low temperatures. The residue is then digested in order to obtain the desirable dietary products heretofore and hereafter described. It is to be understood that both the water and the fat in the aforesaid and related processes may be extracted with acetone in place of or in addition to the treating agents previously described or suggested therefor.

If desired, the fat content of the invertebrata may be extracted continuously during digestion of the comminuted flesh. This may be accomplished, for example, by continuously treating the digested material with a fat solvent and continuously withdrawing therefrom the fat solvent with its extracted fatty content. One of the many practical methods of accomplishing this is to introduce petroleum ether vapors into the bottom of the digestion vessel, under the digestion liquid. This vapor may be introduced through a plurality of small apertures. Upon striking the digestion liquid the vapor is condensed into tiny droplets which ascend through the digesting mass dissolving the fat present therein. The petroleum ether, with its fat content, may then be withdrawn from the top of the digestion vessel.

Removal of provitamin D after the invertebrata has been digested is also contemplated. In this connection, it should be mentioned that the major portion of the fat, which contains the provitamin D, is generally found in the indigestible residue of the digestion mass. The provitamin content of this fat depends to a certain extent upon the conditions of digestion. For instance, if digestion takes place at a pH of 4, a smaller amount of the provitamin D is destroyed than if the digestion is carried out at a pH of 1. On the other hand, when digestion is conducted at a pH above 4, a larger amount of decomposition products which have a somewhat unpleasant taste and/or smell are produced than if a lower pH (between 4 and 1) is used. Likewise, at a pH of about 4 approximately 75% of the albumen present is digested, at a pH of about 3 approximately 60% of the albumen is digested, at a pH of about 2 but 40% of the albumen is digested. It, therefore, appears that as the pH value of the digestion solution is lowered the amount of albumen digested is decreased. In view of the aforesaid considerations it is recommended that particularly where the provitamin D is still present in the material undergoing digestion should be carried on at a pH which is maintained at or close below 4. By following this recommendation the provitamin D content is preserved without serious impairment. When the invention, is carried out without the special object of obtaining a maximum amount of provitamin after digestion; it is not necessary to maintain the pH at or near to pH=4. Digestion in the whole range of pH between 1 and 4 produces a solution suitable for dialyzation without undue loss of valuable constituents and the production of by-products having an unpleasant taste or smell is largely avoided.

Digestion is generally carried on in an acid medium, but it is understood that this medium may be obtained and maintained without the use of the specific acid heretofore referred to. In place thereof, or in addition thereto, other well known acids may be utilized. Likewise, it is contemplated that catalysts or other materials capable of accelerating and/or controlling the digestion reaction may be introduced into the digestion vessel.

While temperatures in the neighborhood of about 37° C. to about 40° C. are preferred for digestion it is understood that the invention is not limited thereto. The particular temperature will depend to a certain extent upon the material undergoing digestion, the condition of this material, the pH value of the digestion solution, and the time of digestion. Temperatures either higher or lower than the aforesaid range may be used, although for best results over a wide range of conditions, temperatures within the limits of 37° C., to 40° C., are considered preferable.

As digestion is seldom, if ever, carried through to completion the digestion mass is generally obtained with an undigested residue content. The undigested residue may be separated from the liquid portion of the resulting mass in the customary manner, for example, by filtering, centrifuging, and the like. If the fat content of the liquid portion is appreciable it is contemplated that this fat may be removed therefrom by suitable fat solvents, particularly where the provitamin D has not been extracted from the invertebrata prior to or during digestion.

Upon the completion of the digestion process the digestion reaction should advisably be terminated by suitable sterilization operations. For example, the digestion mass may be heated for a short period to a temperature of about 100° C. This particular sterilization treatment not only has the advantage of completing the digestion reaction but also it assists in the separation of the undigested residue from the liquor of the digestion mass.

When the liquor of the digestion mass is separated from the undigested residue it is found to contain the larger portion of the albumen decomposition products. This liquor may be further purified by dialysis, if desired. Whether or not the digestion liquor is dialyzed will depend to a great extent upon the particular material digested, the process of digestion and the taste of the individual. If a large amount of salts or undesirable decomposition products should be present in the digestion liquor then dialyzation is, as a rule, advisable for their removal.

In order to obtain the desirable dietary product the digestion liquor may finally be evaporated to dryness. Before evaporation it is generally advisable to raise the pH value of this liquor as this improves the taste of the resulting product. An increase in the pH to approximately the neutralization level is ordinarily advisable, although it is not essential. Evaporation of the liquor should advisably take place under vacuum

in order that harmful decomposition of the desirable products will not result. An evaporation temperature no higher than about 50° C. is customarily preferable, and the vacuum should be selected with such temperatures in mind. For this evaporation operation other well known expedients may also be utilized as, for illustration, a vacuum drum drier or a spray drier operating at low temperatures.

The resulting dry products have a pleasing taste and high nutritive value. They may be used to produce desirable articles for human consumption in the same manner as extracts of meat and various cereal products have heretofore been used. Where these products contain provitamin D it is contemplated that the provitamin may be antirachitically activated, for instance, by suitable treatment with ultra violet light or other activating media. Activation of the provitamin D content may take place either before or after the dietary product is obtained in dry form. Such activation increases the dietary value of the product by adding the antirachitic factor to the other nourishing constituents thereof. If desired, the vitamin D content may be increased by the addition thereto of preformed vitamin D or, in the alternative, additional provitamin D might be added thereto and the product thereafter antirachitically activated. In the same manner, the product may be mixed with other materials having dietary value such as other vitamins or minerals.

By means of the present invention a new series of palatable and nourishing dietary products are made available. These products are produced from an abundant source at a very low cost. The products are palatable and can be used as an important part of the human diet. At the same time as these products are obtained a large amount of valuable provitamin D may be separated from the material without unduly harming either the provitamin D or the ultimate dietary product.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

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