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RECOVERY OF STEROLS

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The present invention relates to the production of sterols and particularly relates to their extraction from plant and animal sources.

It is known that sterols occur in many vegetable and animal products associated with fats and oils. Soy bean oil contains an appreciable though small amount of sterols consisting principally of stigmasterol (16–20%) and larger amounts of sitosterol (84–80%). The tall oil soaps and tall oil obtained from the digestion of wood pulp also contain an appreciable quantity of sterols, particularly sitosterol. Yeast is another common source of sterols, ergosterol being the principal one. Cholesterol is of animal origin and occurs in all animal tissues. These sterols occur in nature, partly in the free condition and partly esterified with higher fatty acids.

The usual methods of isolation involve subjecting the fatty fraction containing the sterols to a saponification step with alkali, preferably an alcoholic alkali solution and extracting the unsaponifiable sterols with a solvent such as ether, trichlorethylene, etc. However, considerable difficulty is encountered in extracting the soap formed, and none of the known methods are sufficiently simple and easy to enable the sterols to be manufactured commercially at a price low enough to encourage their use.

The soaps formed are of a gummy, heavy nature from which it is hard to extract all of the sterols. They are not of such a nature that they can be extracted by a continuous process, and large amounts of solvent are necessary. The saponified material may be shaken with the solvent to facilitate the extraction but this results in the formation of stiff emulsions which are difficult to separate, the only feasible procedure being to use large amounts of solvent and to dilute the solvent layer above the emulsion since a large amount of solvent is retained in the emulsion. When drying of the soap is attempted other difficulties are encountered. As is known the drying of soaps is a difficult procedure and when vacuum drying is resorted to, there is a large amount of foaming and bubbling over of the foam.

In the latest published method of recovering sterols from soy bean oil Reichstein and Steiger, Helv. Chim. Acta. 20, 1043 (1937), employ repeated shaking out of the soap with solvent, followed by repeated washings of the extract. As is readily apparent this involves the use of much solvent, much time, and many operations, and greatly increases the cost of the sterols, which are at best only recovered in a small percentage of the original material treated. Since interest in the sterols has recently been greatly increased due to the synthesis of sex harmones from sterols by several workers a practical method of recovery is desirable.

According to the present invention a method is provided whereby the sterols may be readily and simply recovered. The method involves a procedure whereby the amount of solvent required for extraction is greatly reduced, the time required for isolation is greatly reduced, and the amounts recovered increased. Moreover, the troubles inherent in the prior art processes are overcome.

According to the present invention the saponified fatty materials containing the sterols are treated with quick lime. Water present in the mixture reacts with the quick lime, the heat produced resulting in converting additional water to steam. The steam generated in situ in the soap causes a puffing of the soap, producing a porous granular mass which is easily extracted with relatively small amounts of solvent. The porous character of the mass enables ready percolation of the solvent with free access of the solvent to all parts of the mass. The soapy material containing the sterols treated in this manner can be readily extracted by a counter current extraction, a continuous extraction such as in a Soxhlet type extractor, or by any other highly efficient extraction method.

The extract can then be evaporated to recover the sterols in a fairly pure form. This fairly pure product may be further purified by crystallization of the sterols from alcohol solution or by other well known purification methods. Before evaporating the extract it is desirable but not necessary to wash the extract with an alkali solution to remove any traces of oil or soap which may be present.

The following examples illustrate the invention:

Example I

200 pounds of a concentrated fraction of soy bean oil containing the sterols was treated with 80 pounds of 50% caustic soda solution, and the mixture heated to about 180° F. for about 15 to 20 minutes, and 100 pounds of quick lime added and the mixture agitated to mix in the quick lime. After a short additional warming the mixture began to puff up, and the agitation was continued. The mixture heated up rapidly, and in a short time the entire mixture had been converted into a dry, crumbly, readily permeable

mass of porous granules. Condensed water vapor could be seen rising from the mass.

This porous granular mass was then extracted with ether, in a Soxhlet type extractor. The ether extract of sterols thus obtained was then washed with 10% caustic soda solution to remove any residual oil or soap and then evaporated to dryness. The crystalline crude sterol mass remaining was then dissolved in ten times its weight of boiling alcohol from which almost colorless crystals of sterols were obtained.

Example II

100 pounds of soy bean oil containing the sterols in higher concentration than in the original oil was heated in a shallow pan to 180° F. 53.2 pounds of 37.5% caustic soda solution was added and the mixture well stirred until a semi-plastic state had been obtained. 29.9 pounds of quick lime is then added and the mixture agitated to insure intimate contact between soaps and quick lime. After a few minutes, the mass begins to swell and puff up. In a short while the mixture is dry and of a porous nature.

The porous mass was then extracted with ether in a Soxhlet extractor. The ether extract was then dropped into hot alcohol, whereupon the ether was evaporated, the sterols went into solution, and the impurities precipitated. After filtering the alcoholic solution hot, it was cooled and the sterols crystallized from solution. The sterols recovered were of substantially 100% purity and consisted principally of stigmasterol and sistosterol.

Example III

To 500 grams of crude tall oil soap containing 31% moisture as obtained from the treatment of wood pulp with caustic, was added 500 grams of quick lime, and the mixture warmed to about 100° C. with agitation. After a few minutes the mixture began to puff up. Due to the excessive heat caused by the large amount of water the mixture was cooled. In a few minutes the entire mass had been converted into a dry crumbly mass of porous granules from which the sterols were extracted and recrystallized as in Example I. About 15 grams of practically colorless once crystallized sterols were obtained.

In place of tall oil soap the tall oil itself as obtainable on the market may be used and first saponified with alkali.

Preferably the soaps used or formed for the treatment with quick lime are liquid or soft soaps, such as sodium and potassium soaps. Harder soaps made with other basic radicals may be used however. Preferably the crude mixture of soap, sterol, and water to which the quick lime is added is of a soft or liquid consistency. Ammonium soaps or other soaps containing moieties volatile at the temperature generated by the reaction of the quick lime with water may be used and the gases so generated aid the puffing action. A dehydrated soap, however, should not be used as the reaction between the quick lime and water will not occur. Any suitable source of raw material containing sterols may be used, such as soy bean oil, Calabar beans, yeast, animal cells, tall oil and its soaps, soybean oil foots, etc.

The amount of lime used should be sufficient to produce the puffing action, and preferably is sufficient to convert into steam all of the water not reacted with the lime. It need not be sufficient to completely form calcium soaps from all of the alkali soaps when such are used. In the examples given the porous granular mass is a mixture of the sodium and calcium soaps containing the sterols. So far as is known the treatment with quick lime does not affect the sterols.

In place of ether, other sterol solvents, which are nonsolvents for soap may be used such as benzol, trichlorethylene, etc.

Having described the invention what is claimed and desired to secure by Letters Patent of the United States is:

1. The process of recovering sterols which comprises providing a crude mixture comprising soaps, sterols and water, mixing sufficient quick lime with said crude mixture to form a porous mass, and then extracting the sterols from said porous mass.

2. The process of recovering sterols which comprises providing a crude mixture containing soaps, sterols and water, mixing sufficient quick lime with said crude mixture to cause substantially complete removal of the water, whereby a porous mass is produced, and extracting the sterols from said porous mass.

3. The process of recovering sterols which comprises providing a crude mixture containing alkali soaps, sterols and water, mixing sufficient quick lime with said crude mixture to form a porous mass, and extracting the sterols from said porous mass.

4. The process of recovering sterols from fatty materials containing the same which comprises saponifying the fatty material, mixing sufficient quick lime with the saponified material to form a porous crumbly mass, and extracting the sterols from said porous mass.

5. The process of recovering sterols from fatty materials containing the same which comprises saponifying the fatty material, mixing sufficient quick lime with the saponified material to cause substantially complete removal of the water present, whereby a porous mass is produced, and extracting the sterols from said porous mass.

6. The process of recovering sterols from fatty materials containing the same which comprises saponifying the fatty material with an alkali saponifying agent, mixing sufficient quick lime with the saponified material to form a porous mass, and extracting the sterols from said porous mass.

7. The process of recovering sterols which comprises saponifying a fatty material of vegetable origin containing sterols, mixing sufficient quick lime with the saponified material to form a porous mass, and extracting the porous mass with a solvent for sterols.

8. The process of recovering sterols which comprises providing a crude mixture containing soap, sterols and water, mixing quick lime with said crude mixture, the amount of quick lime being sufficient to cause substantial evaporation of sensible water from the mass whereby it is converted into a porous mass and extracting the sterols from said porous mass.

9. As an improvement in the process of recovering sterols from saponified material containing the same by an extraction method, the step which comprises mixing sufficient quick lime with the saponified material before drying or extracting the same to form a porous mass.

10. The process of recovering sterols which comprises providing a crude mixture containing soaps, sterols and water, mixing sufficient quick lime with said crude mixture to cause substantial evaporation of water and to convert the mixture into a porous mass, extracting the sterols from said porous mass, washing the extract with an

alkali solution, and recovering the sterols from the washed extract.

11. The process of recovering sterols which comprises providing a crude mixture of soft consistency of soap, sterols and water, mixing sufficient quick lime with said crude mixture to form a porous mass, and extracting sterols from said porous mass.

12. In the process of recovering sterols the steps which comprise providing a crude mixture of soap, sterols and water and mixing quick lime with said crude mixture, said soap mixture containing an ingredient in addition to the water which is volatile at the temperatures generated by the reaction of the quick lime and water whereby the steam formed and the gas generated by the heat of the reaction between the quick lime and water produces a porous mass readily extractible by solvents.

13. The process of recovering sterols from soy bean oil containing the same which comprises saponifying the oil with an aqueous caustic alkali solution, adding sufficient quick lime to the soaps thus formed to produce a porous mass, and extracting the porous mass with a solvent for sterols which is a non-solvent for soaps.

14. The process of extraction comprising the steps of first providing a crude mixture of soap, water and a substance to be extracted, adding sufficient quick lime to the crude mixture to form a porous mass, and then extracting the porous mass with a solvent for the material to be extracted which is a nonsolvent for soap.

15. The method of recovering sterols from fatty materials containing the same which comprises converting the fatty materials to soap, sufficient amounts of quick lime and water being reacted in the process to generate steam and to form a dry crumbly porous mass readily percolated by solvents, and extracting the sterols from the porous mass.

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