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RECOVERY OF STEROLS

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This invention relates to the recovery of sterols, and more particularly, to the recovery of sterols from phosphatidic material.

Crude vegetable oils, such as cottonseed oil, corn oil, soyabean oil, peanut oil, linseed oil and rapeseed oil, etc., usually contain substantial amounts of phosphatidic material. This is true irrespective of whether the oil is recovered from the oil seeds by solvent extraction or by pressing operations. Such phosphatidic material may be recovered from the crude oil by adding a small amount of water to the oil to precipitate the phosphatidic material therein and then continuously centrifugally separating the precipitated material from the oil. Such a process is carried out commercially on a large scale for the recovery of phosphatidic material from corn oil and soyabean oil. The recovered phosphatidic material is dried under vacuum and at a moderate temperature. The dried phosphatidic material is the usual commercial product and contains an amount of the original oil ranging between approximately 30 and 40% of the weight of the dried material as a carrier. The phosphatidic material from soyabean oil and corn oil is largely used in edible products and is relatively inexpensive since it is a by-product and the amount which could be recovered exceeds the demand. Phosphatidic materials from certain other edible oils, such as peanut oil, are suitable for the same purposes but, so far as applicant is aware, are not produced commercially. The phosphatidic material from cottonseed oil is, in general, not suitable for edible purposes as it contains a difficultly removable toxic material, gossypol. The phosphatidic materials originally present in cottonseed oil and those in many of the other edible oils, as well as those in non-edible vegetable oils such as those employed in paints, are discarded as waste materials from the oils in the various refining procedures employed thereon.

The phosphatidic materials which may be obtained from any of the above oils by the process described above or similar processes constitute an excellent source for the recovery of sterols in accordance with the process of the present invention. Such phosphatidic material will usually contain between 4 and 5% of sterols based on the weight of the oil-free phosphatidic material. The starting materials for the process of the present invention may either be the crude phosphatidic material referred to above after such material has been dried to remove substantially all water, or they may be such dried phosphatidic material from which the carrier oil has been removed by solvent treatment. That is to say, substantially all of the sterols remain in the phosphatidic material even though the carrier oil has been removed therefrom by treatment of the dried crude phosphatidic material with a solvent for the oil which is not a solvent for the phosphatides. The sterols appear to be present in the phosphatidic materials as sterol glycosides and perhaps other sterol compounds in complex combination with phosphatides as neither the sterol glycosides nor sterols themselves are liberated from the phosphatidic material in any process which does not break down the phosphatidic molecules.

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It is an object of the present invention to provide an improved process of recovering sterols from phosphatidic material.

Another object of the invention is to provide an improved process of recovering sterols from phosphatidic material in which the material is treated in a manner to not only break down the phosphatide molecules but also any other sterol compounds so as to enable the recovery of sterols in substantially pure form.

Other objects and advantages of the invention will appear in the following detailed description of the process.

As stated above, either the dried crude phosphatidic materials or the oil-free phosphatidic materials from any of the vegetable oils discussed above constitute suitable starting materials for the process of the present invention. In carrying out the process of the present invention, these materials are first refluxed with an alcoholic acid, preferably methanolic hydrochloric acid or methanolic sulfuric acid, although other alcohols and other strong acids can be employed. Thus phosphoric acid may also be employed. The acid need not be an inorganic acid as strong organic acids such as trichloroacetic and alkyl and aryl sulfonic acids can be employed. The important properties of the acids are that they should not be more oxidizing than sulfuric acid and should not decompose at the temperature employed in the reaction. Nitric acid, for example, is not suitable as it has too strong an oxidizing action.

As to the alcohols employed, methanol is the preferred alcohol but aliphatic alcohols up to amyl alcohol may be employed, i. e., aliphatic alcohols having not more than 5 carbon atoms. The temperature employed will ordinarily be the reflux temperature of the alcohol at atmospheric pressure, i. e., a temperature ranging from 64° C.

to 138° C., although treatment under pressure may be employed at temperatures ranging from approximately 64° to 150° C. Mixtures of alcohols may, of course, be employed with any of the acids above mentioned and similarly, mixtures of acids with any of the alcohols or mixtures thereof may be employed.

The time of treatment of the phosphatidic material with the alcoholic acid will vary between ½ and 12 hours, and will preferably be between 6 to 10 hours. The acid will ordinarily be employed in a large excess, i. e., an amount of concentrated acid by weight equal to ½ to 2 times the amount of phosphatidic material. In the case of hydrochloric acid, the weight referred to is the weight of anhydrous hydrochloric acid dissolved in the alcohol. The amount of alcohol employed will ordinarily range from approximately 10 times to 40 times the volume of phosphatidic material. Under the above conditions, substantially all of the esters and sterol glycosides will be split and the sterols are liberated.

In most cases, all of the phosphatidic material will go into solution but if any insoluble materials remain, the solution may be filtered hot, i. e., at approximately the reflux temperature of the alcohol employed. The solution is usually thereafter concentrated by evaporation of the alcohol to a volume ranging from 10 to 20 times that of the original phosphatidic material. Upon cooling to room temperature, i. e., approximately 20° C., or below, and preferably to a temperature between 0° and 10° C., the sterols precipitate as crystals. The cooled solution is again filtered and the residue of sterol crystals washed with an alcohol at approximately room temperature or below, i. e., from 0° to 20° C. Centrifugal separation instead of filtration can be employed to separate the crystals from the mother liquor. The filtrate or mother liquor is largely a solution of alcoholic esters of fatty acids although the solution contains a substantial amount of decomposition products of the phosphatidic material and small amounts of other materials such as glycerin and unsplit glycosides. By adding water to the filtrate the alcoholic esters of the fatty acids collect as an upper layer and may be separately recovered by decantation.

The crude sterol crystals may be further purified by recrystallization employing any of the alcohols which may be employed in the alcoholic-acid treatment. The recrystallization is performed by dissolving the sterol crystals in the alcohol at substantially the boiling temperature of the alcohol and then cooling and separating the crystals as above described. A yield of purified sterol crystals is recovered in an amount ranging from approximately 4 to 5% of the weight of the original phosphatidic material.

As a specific example, 7 parts by weight of oil-free corn oil phosphatidic material were refluxed in a solution made up of about 3.6 parts by weight of concentrated sulfuric acid in a volume of methyl alcohol equal to about 20 times that of the phosphatidic material for 8 hours. At the end of this time the resulting solution was filtered hot and the filtrate concentrated to approximately one-half its volume by boiling off the alcohol. The resulting solution was cooled to room temperature and the resulting crude sterol crystals filtered from the solution. These crystals were then washed with approximately 100 times their volume of methyl alcohol at room temperature after which they were dissolved in approximately 10 times their volume of methyl alcohol at approximately 68° C., and the resulting solution again cooled to room temperature. Sterol crystals were again precipitated and filtered therefrom to produce a yield of approximately 35 parts by weight of substantially pure sterols.

The nature of the sterols recovered will depend upon the nature of the oil from which the phosphatidic material was originally recovered. In the case of corn oil phosphatidic material, the sterols will be predominantly alpha, beta and gamma sitosterol with small amounts of sitostanol, stigmasterol and other sterols, while in the case of soyabean phosphatidic material, the sterols will contain significant amounts of stigmasterol.

We claim:

1. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an excess of a strong non-oxidizing acid in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being sufficient to dissolve the resulting products at said temperature, thereafter cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

2. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an amount of a strong non-oxidizing acid equal to ½ to 2 times the weight of said phosphatidic material in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being sufficient to dissolve the resulting products at said temperature, thereafter cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

3. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an amount of a strong non-oxidizing acid equal to ½ to 2 times the weight of said phosphatidic material in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C and 150° C. for sufficient time to decompose the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being between 10 and 40 times the volume of said phosphatidic material and being sufficient to dissolve the resulting products at said temperature, thereafter cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

4. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an excess of a strong non-oxidizing acid in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose

the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being between 10 and 40 times the volume of said phosphatidic material and being sufficient to dissolve the resulting products at said temperature, thereafter cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

5. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an excess of a strong non-oxidizing acid in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being between 10 and 40 times the volume of said phosphatidic material and being sufficient to dissolve the resulting products at said temperature, thereafter concentrating said resulting solution to a volume ranging between 10 and 20 times the volume of the original phosphatidic material by evaporation of alcohol, cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

6. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an excess of hydrochloric acid in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose the phosphatides of phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being sufficient to dissolve the resulting products at said temperature, thereafter cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause

crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

7. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an excess of sulfuric acid in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being sufficient to dissolve the resulting products at said temperature, thereafter cooling the resulting solution to a temperature between approximately 0° and 20° C. to cause crystallization of crystals of said sterols, and separating said crystals from the cooled solution.

8. The method of recovering sterols from vegetable oil phosphatidic material, which comprises, treating said material with an excess of a strong non-oxidizing acid in a lower aliphatic alcohol containing not more than 5 carbon atoms and at a temperature between approximately 64° C. and 150° C. for sufficient time to decompose the phosphatides of said phosphatidic material and liberate substantially all of the sterols, the amount of alcohol being sufficient to dissolve the sterols at such temperature, and recovering sterols from said solution.

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