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## PROCESS FOR RECOVERING STEROLS

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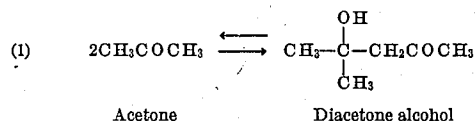
The present invention relates to the recovery of sterols and particularly to the recovery of sterols which are found in oil-bearing seeds such as soybean, cotton seed, etc. It is also applicable with certain alterations to the extraction of sterols from Tall Oil and the juices and saps secured by pressing certain plants, among which may be mentioned sugar cane.

In the recovery of sterols it is conventional to seek to use as raw material the oil pressed out of oil bearing seeds inasmuch as the most of the sterols dissolve in the oil when it is either pressed out or extracted from such seeds. The conventional method of working up this oil has been to convert the oil into a soap, and to extract from said soap the unsaponifiables consisting of sterols along with waxes, etc. The amount of unsaponifiables present in the oils varies from oil to oil. In soybean oil the usual figure is given as 0.8%. Figures, however, have been obtained ranging from 0.5 to 1.6% when the determinations are made by the official method of the Association of Official Agricultural Chemists. In extracting the sterols from the soap the conventional method has been to dissolve the soap in alcohol, or to form the soap with alcoholic alkali, and to shake out the resulting soap solution with water-immiscible solvents such as ether, benzene, ethylene dichloride, petroleum ether, carbon tetrachloride, etc. These reagents extract as a general rule not only the sterols but also most of the other unsaponifiables which represent materials of a gummy or wax-like nature. For this reason such a method is commonly employed in a quantitative determination of the percentage of unsaponifiables in the oil. Naturally the extract contains some alcohol and therefore some dissolved soap and is washed frequently with water and alkali to remove alcohol and soap. Even after such washing, which constitutes a laborious procedure and is difficult to carry out on a large scale, there remain in the washed extract the gummy and waxy material spoken of above and these interfere seriously with the crystallization of the sterols from said extract. For a clean crystallization of the sterols, these materials are best removed before crystallization. For example, when ether is used as the extract, the washed ether extract may be concentrated, and the addition of hot alcohol to the concentrate throws down a large amount of gummy material. If this is removed immediately by filtration (difficult in this case) the sterols will usually crystallize, from the ether extract. Ethyl ether is, however, a difficult solvent to use in a commercial extraction of sterols, first because of the large volumes which are required and because of the hazard in employing a solvent like ethyl ether. Isopropyl ether has been recommended,

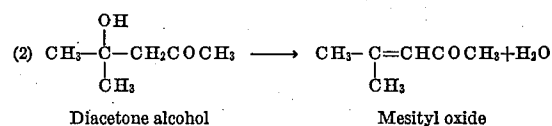
It, however, forms explosive peroxides unless inhibitors are added and the maintenance of these inhibitors in the distilled solvent is difficult and fraught with dangers.

According to the present invention, a method is provided whereby the sterols may be recovered by a simplified procedure. It is the purpose of the present invention to employ a solvent which will extract substantially only the sterol portion of the unsaponifiables and leave behind certain objectionable gummy and wax-like materials which are usually extracted along with the sterols when extracted in accordance with every published method for extracting the sterols. For this purpose we have found water-miscible volatile ketones such as acetone, methyl ethyl ketone especially suitable. Moreover these water-miscible volatile ketones are superior to the usual water immiscible solvents employed for the extraction of sterols, because—in addition to leaving behind much gummy and wax-like material—they do not swell a solid lime soap such as described in application Serial No. 266,408, and which soap has been shown to be very superior to the usual alcoholic solutions of a soap as starting material for the extraction of sterols. Solvents like ether, benzene, and the chlorinated solvents swell these "lime soaps" decreasing somewhat the ease of filtering or percolation through these inherently easily extractable soaps. Water miscible ketones like acetone tend to dry the soap and the solvent therefore filters through or percolates through the soap with great ease and thorough and quick extraction of the sterols is made possible.

Acetone in the presence of basic substances is reversibly converted to diacetone alcohol according to Equation 1



Diacetone alcohol in the absence of the basic substances in whose presence Equation 1 is reversible, loses a molecule of water to form mesityl oxide by a nonreversible reaction according to Equation 2



Similar reactions occur in the case of methyl-ethyl ketone and similar ketones (Organic Syntheses, vol. 1, p. 193, John Wiley Sons, New York, 1932).

In extracting soap with acetone the conditions are present which result in the reaction of Equa-

tion 1 taking place. After the extract of the sterols is drained away from the soaps there is no base present to catalyze Reaction 1. Since acetone is more volatile than diacetone alcohol, evaporation of the acetone will result in an accumulation of diacetone alcohol and mesityl oxide at the point of evaporation, and if continuous or successive concentrations are employed the condition is aggravated so that there is formed a syrupy mixture of diacetone alcohol, mesityl oxide and sterols.

By conducting the evaporation under the conditions of Equation 1 (i. e. in the presence of basic substances to catalyze the reversible reaction) the removal of the acetone causes Reaction 1 to go to the left and a minimum formation of mesityl oxide results, substantially no diacetone alcohol remaining in the evaporated extract. Any basic substances such as alkalis and organic bases may be used. It is good practice to use a basic substance which is subsequently easily removed, as for example barium hydroxide.

The evaporation may be carried down until an oily mass is formed, which in addition to the sterols contains a small amount of mesityl oxide, a small quantity of unsaponified oil, a small quantity of soap carried over as fines or in the form of soluble soaps and the added base whose purpose is discussed above.

The dry "lime soaps" as described in the Serial No. 266,408, filed April 6, 1939—and which soaps have been made by treating a wet aqueous concentrated soap with sufficient quick lime to cause the drying and puffing of the soap due to the formation of steam by the heat of reaction between water and quick lime—are the preferred soaps for such an extraction with water miscible ketones. The procedure, however, can be applied to any dry soap such as a vacuum dried soap, or a soap dried on drums. Such dry soaps may be made from ordinary soybean oil, ordinary cottonseed oil or from other vegetable and animal sources and is advantageously treated in accordance with the present invention to recover the sterols therefrom.

In addition to the ordinary oils, concentrated fractions of oils may also be employed, such as the "concentrate" secured by scrubbing oils with alcohol. As is well known most oils are only partially miscible with ethyl and methyl alcohol. The unsaponifiables in such oils dissolve readily in these alcohols in the presence of small quantities of oil. Thus when the oil is scrubbed with the alcohols the latter become quickly saturated with oil and the most of the unsaponifiables leave the oil and go into the alcohol phase which forms a separate layer and can be drawn off from the oil layer. Thus, on evaporation of the alcohol, an oil more concentrated in sterols than the original oil is obtained. This is the "concentrate" referred to in this paragraph. This procedure is described in Circular No. 212, from the United States Department of Agriculture, Bureau of Animal Industry, and is employed as a tentative method for formation of oil concentrates containing Cholesterol and Phytosterol as described in "Official and Tentative Methods of Analyses of the Association of the Official Agricultural Chemists" in the 1930 edition of this book, page 327. Dry lime soaps made from such concentrates of vegetable and animal oils are easily extracted by the method employed in the present invention and indeed this method constitutes what is considered a

novel and greatly improved method of securing sterols from such concentrates.

In addition to ordinary oils and the concentrates of such oils, it has been found that the method of the present invention works well with the "sludge" secured on the alkali refining of vegetable and animal oils. In this alkali refining aqueous alkali is added to the oil under agitation and a "sludge" containing phosphatides and unsaponifiables is thrown down. This "sludge" usually contains from 40 to 50% water. Such a sludge as is drawn off of the alkali refining tanks can be treated with a small quantity of flake caustic to complete saponification and then with a quantity of quick lime (depending upon the amount of water present) to form a dry crumbly and porous soap. This soap is very conveniently extracted with water miscible ketones according to the method of the present invention and the use of such material permits a cheap recovery of the sterols therein.

High acid oil or other sterol containing residues resulting from the purification of phosphatides such as soybean phosphatides, cottonseed phosphatides, etc. may also be used as raw material.

In addition to all of the above raw materials sterol containing distillation residues secured on rectifying the fatty acids may be converted into dry lime soaps and extracted according to the method of the present invention.

Particularly useful is the method of the present invention in working up a residue such as secured by Kraybill and others in U. S. Patent No. 2,174,177. This method adsorbs the sterols and phosphatides onto an adsorbent consisting of sodium and aluminum silicate. When this adsorbent is washed with acetone there is secured an acetone solution substantially free of phosphatides, which are insoluble therein, consisting of a goodly portion of oil containing sterols. This is another method of securing a concentrate. Such a concentrate is most conveniently worked up for recovery of sterols by converting it into the dry lime soap discussed above and extracting according to the method of the present invention.

The method of the present invention is also particularly applicable the concentrated oil solution of unsaponifiables secured on the molecular distillation of vegetable and animal oils such as described by H. W. Rawlings in Oil and Soap, December 1939, volume 16, number 12, page 231. This concentrate is readily convertible into a dry lime soap for extraction according to the method of the present invention. This results in saving of time and in much more quantitative recovery of sterols than any other known commercial method.

#### Example I

400# of a concentrated soybean oil was converted to 600# of dried soap according to the aforementioned application Serial No. 266,408. This soap was then extracted six times in an extractor of the percolator type with 500-600 gallons of acetone, and the acetone drained off to a still which had been charged with 1# of barium hydroxide. This amount of barium hydroxide is sufficient for 10-20 extractions or more, if none is drawn off, since it acts as a catalyst and is not used up in the concentration. The extract was distilled down to an oily mass which contained the sterols, a small amount of mesityl oxide, a small quantity of soap carried over as fines or in the form of water soluble

soap, a small quantity of unsaponified oil, and pigment impurities.

The extract thus obtained was concentrated to about 1½ gallons and taken up in about ½ its volume of hot glacial acetic acid. This solution was slowly cooled, the sterols crystallizing out in large crystals which were easily filtered or centrifuged. The crystalline sterols may then be washed with methyl alcohol and recovered as practically colorless crystals consisting of about 3 to 5# of substantially pure soybean sterols having a melting point of 131° C.-133° C.

#### Example II

245 grams of porous lime soap of soybean oil was extracted with methyl-ethyl ketone in a Soxhlet extractor, the soap being covered with the hot ketone and drained eight times, one gram of Ba(OH)<sub>2</sub> and 800 cc. of the ketone being used in the boiling flask. The extract was concentrated to a small volume and crystallized after addition of a few cc. of acetic acid. The first crop of sterol crystals after washing with methyl alcohol were nearly white, weighed 1.4 grams and melted at 130-132° C.

#### Example III

670# of sludge from the alkali refining of soybean oil were treated with 30 pounds of caustic flakes using good mechanical agitation. This action insured complete saponification of all free oil present. 280# of quick lime were mixed into the soft plastic mass with mechanical agitation to insure a homogeneous mixture. Within a few minutes, puffing and swelling occurred and the soap dried to a granular porous mass. This mass was placed in an extractor and extracted with acetone. The acetone extract was concentrated under vacuo yielding 6 gallons of extract. The concentrated extract was worked up for the recovery of the sterols therefrom. A yield of 3.81 pounds of sterols was obtained, representing a yield of 0.57% based upon the weight of sludge.

#### Example IV

670# of sludge from the alkali refining of cottonseed oil were treated with 20.7# caustic flakes in the same manner as described above. The mass was treated with 241 pounds of quick lime as described above. The soap was extracted in the usual manner, yielding 6 gallons of extract. Upon working up the extract for the recovery of the sterols 3.69 pounds of sterols were isolated. Based upon the weight of foots processed, this represented a yield of 0.55%.

A previously pointed out other volatile ketones than acetone and methyl-ethyl ketone may be used. However, they should be sufficiently volatile to permit ready concentration of the extract by evaporation or distillation. The basic substances are preferably alkalis but organic bases may be used.

While the use of dry porous soaps such as the dry lime soaps referred to are preferable, in general any substantially dry and substantially oil-free material containing sterols and basic substances may be treated in accordance with the present invention for the recovery of sterols.

When using dry lime soaps it is preferable to dry the soap down to a moisture content of about 2% by the Dean-Stark method. This method will not remove water from calcium hydroxide or hydrated calcium chloride and will only show up excess water not combined with calcium oxide. When the amount of free water exceeds 3%, ap-

preciable quantities of soap may be dissolved in the acetone or other water miscible ketone. Thus it is preferable to keep the moisture content of the soap in the neighborhood of 2 to 3%, as this renders subsequent purification easier. The invention, however, is not limited to these percentages as extracts free from other unsaponifiables, etc. may be obtained when extracting materials containing other percentages of water.

We claim:

1. The process of recovering sterols which comprises extracting substantially dry, substantially oil-free soybean material containing sterols and a basic substance with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance.

2. The process of recovering sterols which comprises extracting substantially dry soybean soap containing sterols with a water miscible volatile ketone, separating the extract from the insoluble residue, and concentrating the extract by evaporating the ketone in the presence of a basic substance.

3. The process of recovering sterols which comprises extracting a porous, dry, lime soap containing sterols with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance.

4. The process of recovering sterols which comprises extracting substantially dry, substantially oil free material containing sterols and a basic substance with a ketone selected from the class consisting of acetone and methyl ethyl ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance.

5. The process of recovering sterols which comprises extracting substantially dry soap containing sterols with a ketone selected from the class consisting of acetone and methyl ethyl ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance.

6. The process of recovering sterols which comprises extracting a porous, dry soap obtained from the sludge resulting from the alkali refining of oils containing sterols with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance.

7. The process of recovering sterols which comprises extracting substantially dry, substantially oil free material containing sterols and an alkaline substance with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of an alkaline substance.

8. The process of recovering sterols which comprises extracting substantially dry soap containing sterols with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of an alkaline substance.

9. The process of recovering sterols which comprises extracting a porous, dry, lime soap containing sterols with a water miscible volatile ketone, separating the extract from the insoluble

residue and concentrating the extract by evaporating the ketone in the presence of an alkaline substance.

10. The process of recovering sterols which comprises extracting sterol containing substantially dry soaps made from the tarry residue remaining upon the distillation of fatty acids with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance. 5 10

11. The process of recovering sterols which comprises extracting sterol containing substantially dry soaps made from the tarry residue remaining upon the distillation of fatty acids with a ketone selected from the class consisting of acetone and methyl ethyl ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the ketone in the presence of a basic substance. 15 20

12. The process of recovering sterols which comprises extracting soaps made from the tarry residue remaining upon the distillation of soya oil fatty acids with a water miscible volatile ketone, separating the extract from the insoluble residue, and concentrating the extract by evaporating the ketone in the presence of an alkaline substance. 25

13. The process of recovering sterols which comprises extracting a porous, dry, lime soap of soybean oil containing sterols with acetone, separating the extract from the insoluble residue, and concentrating the extract by evaporating the acetone in the presence of barium hydroxide. 30

14. The process of recovering sterols which comprises extracting a porous, dry, lime soap of soybean oil containing sterols with methyl ethyl ketone, separating the extract from the insoluble residue and concentrating the extract by evaporating the methyl ethyl ketone in the presence of barium hydroxide. 35 40

15. The process of recovering sterols which comprises extracting substantially dry, substantially oil free soybean material containing sterols and a basic substance with a water miscible volatile ketone, separating the extract from the insoluble residue, concentrating the extract by evaporating the ketone in the presence of a basic substance and recovering the sterols from the thus concentrated extract.

16. The process of recovering sterols comprising concentrating a volatile water miscible ketone extract of sterols by evaporating said extract in the presence of a basic substance.

17. The process of recovering sterols which comprises extracting a substantially dry, substantially oil free material containing sterols and a basic substance with a water miscible volatile ketone, separating the extract from the insoluble residue, and concentrating the extract by evaporation in the presence of a basic substance. 20

18. The process of claim 17 in which the material extracted is substantially dry soap.

19. The process of recovering sterols which comprises forming a substantially dry soap from a glyceride oil concentrate containing sterols, extracting said soap with a water miscible volatile ketone, separating the extract from the insoluble residue and concentrating said extract by evaporation in the presence of a basic substance. 25 30

20. The process of recovering sterols from the sludge resulting from the alkali refining of cottonseed oil which comprises converting said sludge into a substantially dry soap, extracting said soap with a water miscible volatile ketone, separating the extract from the insoluble residue, and concentrating said extract by evaporation in the presence of a basic substance. 35 40

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