Patented Dec. 2, 1947 2,432,021

UNITED STATES PATENT OFFICE

2,432,021

CONCENTRATION OF VITAMIN A CAROTENOIDS

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No Drawing. Application April 6, 1944, Serial No. 529,855

10 Claims. (Cl. 167—81)

1

This invention relates to an improved method for concentrating vitamin A carotenoids. More particularly the invention relates to an improved method for treating fatty oils containing vitamin A carotenoids to effect the separation therefrom of fractions containing vitamin A carotenoids in higher concentration than in the original fatty oils.

The vitamin A carotenoids are those carotenoids which are capable of being converted to vitamin A, as by hydrolysis. These include alpha carotene, beta carotene, gamma carotene, and cryptoxanthene. These compounds are converted by hydrolysis in animal bodies to vitamin A. One molecule of beta carotene is converted to two molecules of vitamin A whereas the other compounds form but one molecule of vitamin A for each molecule of the original compound. These carotenoids which are capable of conversion to vitamin A are otherwise identified as provitamins A.

The above carotenoids appear singly or in admixture in plants. With few exceptions they are generally absent from animal organisms. The most important sources of these carotenes are the green and yellow parts of vegetables and fruits and certain vegetable oils such as red palm oil. The carotenoids may be obtained from the plant sources thereof, in solution in fatty oils, by pressing or by extraction with a solvent. It is to the concentration of such fatty oils containing the vitamin A carotenoids that the present invention is directed.

Since red palm oil is the most abundant fatty oil containing vitamin A carotenoids the invention is particularly applicable to the treatment of that oil. In the further description of the invention reference will be made, by way of example, to the treatment of that oil. It is to be understood, however, that the invention is applicable to the treatment of any fatty oil containing vitamin A carotenoids to produce concentrates thereof.

The improved method involves in general the treatment of the fatty oil at moderate or low temperatures by means of a selective solvent under conditions effective to maintain the solvent in a liquid condition and under which the solvent and oil form solvent and oil phases between which the oil is distributed. The phases are separated and the oil component of the oil phase is recovered as vitamin A carotenoid concentrate.

The solvents which may be employed include relatively inert fluids which are relatively low boiling and in which the oil is sufficiently soluble to effect extraction of a substantial proportion of the oil. The preferred solvents may be designated generally as those having critical temperatures not substantially higher than 450° F.

To carry out the concentrating step under conditions of the greatest efficiency it is desired to operate at temperatures at which the solubility of the oil in the solvent decreases with rising temperature. This condition occurs generally in the range of temperatures extending from 100° F. below the critical temperature of the solvent to a few degrees above the critical temperature. Operating in this temperature range, and particularly at temperatures close to the critical temperature, requires the use of solvents whose critical temperatures are substantially lower than temperatures which are destructive of the vitamin A potency of the oil. The preferred solvents include those whose critical temperatures are below 325° F. In this group normally gaseous solvents are preferred because of the relative ease with which they are separated from the oil after the treatment as well as for the low operating temperatures which they permit.

2

The low boiling hydrocarbons represent a desirable class of solvents because of their relative inertness and low cost. While the low boiling olefin hydrocarbons may be employed they are less desirable than the low boiling paraffins such as ethane, propane, the butanes, the pentanes and the hexanes, from the point of view of inertness. Of the paraffins, propane is preferred ordinarily because of the high degree of solubility of the oils in that solvent. However, ethane or the butanes can be employed to almost as great advantage. While relatively pure hydrocarbons are preferred mixtures of them may be employed. For example, mixtures of ethane and propane or mixtures of butane and methane may be employed in the proportions suitable to form solvents having the desired properties. While the low boiling hydrocarbons are particularly advantageous for use as solvents in the improved method other solvents having relatively low critical temperatures may be employed, such as ammonia, dichlordifluor methane, dimethyl ether, methyl fluoride and halogenated hydrocarbons in general.

In the further description of the invention propane will be referred to as the solvent. It will be understood, however, that propane merely exemplifies many solvents which may be employed under proper conditions of temperature and pressure and that the general principles of the invention, as exemplified by the use of propane, are applicable in the use of such other solvents.

In the preferred method of carrying out the process the fatty oil containing a vitamin A carotenoid, such as red palm oil, is subjected to counter-current contact with the liquefied propane to increase the efficiency of concentration of the carotenoid content of the oil. Preferably the extraction step is carried out in a countercurrent extraction zone which is refluxed by oil separated from the extract phase. Refluxing may be effected by passing the extract phase through

a rectification zone in which reflux is formed by heating the propane phase to a higher temperature to cause precipitation of oil. Instead of or in addition to the heating step the propane phase, after withdrawal from the extraction zone, is treated to separate propane therefrom and residual oil thus obtained is returned to the rectification zone as reflux. Rectification in this manner is desirable as it promotes the exclusion of the carotenoids from the extract phase and improves the recovery of these desired materials in the oil phase. It will be understood, however, that the invention includes within its scope contacting the solvent and the fatty oil under any conditions effective to form a separate phase containing a portion of the oil having a higher concentration of the vitamin A carotenoids than the original oil.

The temperatures employed ordinarily fall within the range of temperatures between the critical temperature and 40° F. below the critical temperature. The pressure employed is necessarily sufficiently high to insure liquid phase conditions during the operation. Since it may be desirable to make some adjustment of the pressure during the operation it is desirable to maintain the pressure at a substantial margin above the minimum necessary to maintain liquid phase conditions. Ordinarily a pressure which is about 50 pounds per square inch higher than the vapor pressure of the solvent at the highest contemplated operating temperature is satisfactory.

A relatively high ratio of solvent to oil is desirable. The ratio of propane to palm oil should be at least 10:1 and higher ratios are desirable, such as 30:1 or 100:1 or higher.

Example.—A commercial red palm oil having a concentration of vitamin A carotenoids equivalent to a vitamin A potency, as determined by the Carr-Price method, of 2730 I. U./gram was subjected to treatment with liquefied propane in a combined extraction and rectification tower having an inside diameter of 2 inches and 18 feet high. The palm oil was charged to the tower at a point 10 feet from the top of the tower at a rate of 1 liter per hour and propane was introduced into the tower at a point 16 feet from the top in a ratio of 50 volumes of propane per volume of palm oil. A uniform temperature was maintained in the tower between the oil charge point and the propane charge point while a temperature gradient of 176° F. to 193° F. was maintained from the oil charge point to the top of the tower. The temperature gradient was maintained to provide rectification of the tower. Under these conditions a bottom phase containing a portion of the oil equivalent to 7.1 weight per cent of the oil charge was obtained. The remainder of the oil charge passed into the propane phase which was withdrawn overhead. The oil phase which separated was withdrawn from the bottom of the tower and separated from accompanying propane. This oil product was found to have a vitamin A potency of 5,270 I. U./gram. The oil product thus obtained represented a marketable provitamin A concentrate while the oil taken overhead with the propane phase was fully utilizable in the processes in which palm oil is ordinarily employed. It was in fact improved as a soap stock as a result of the concentration of the color bodies of the oil in the bottom oil product.

I claim:

1. A method for concentrating the vitamin A carotenoid content of palm oil which comprises continuously passing said palm oil and liquid propane through an elongated extraction zone in counter-current contact at temperatures not substantially higher than the critical temperature of propane and not substantially lower than 40° F. below said critical temperature, introducing said palm oil and liquid propane into said extraction zone in ratios of propane to palm oil of not less than 10:1, refluxing the extraction zone near the exit for the extract phase by means of oil separated from the extract phase, separately withdrawing final extract and raffinate phases from said zone, separating propane from the raffinate phase thus withdrawn, and recovering from the raffinate a vitamin A carotenoid concentrate.

2. A method for concentrating the vitamin A carotenoid content of a fatty oil which comprises contacting said oil with a low-boiling solvent for said oil, said solvent having a critical temperature not substantially higher than 450° F., the temperature of contact being within the range at which the solubility of the oil in the solvent decreases with rising temperature and between about 100° F. below the critical temperature of the solvent and not substantially above said critical temperature so as to form solvent and oil phases between which the oil is distributed, and the pressure being at least sufficient to maintain the solvent in the liquid phase at the temperature employed, and recovering from said oil phase vitamin A carotenoid concentrate.

3. A method as claimed in claim 2 in which the temperature of contact is within the range of from about 40° F. below the critical temperature of the solvent and not substantially above said critical temperature.

4. A method as claimed in claim 2 in which the solvent and oil are contacted at a temperature above the normal boiling point of the solvent.

5. A method as claimed in claim 2 in which the solvent is gaseous under normal conditions of temperature and pressure.

6. A method as claimed in claim 2 in which the solvent has a critical temperature lower than 325° F.

7. A method as claimed in claim 2 in which the solvent is propane.

8. A method as claimed in claim 2 in which the fatty oil to be treated is palm oil.

9. A method as claimed in claim 2 in which the solvent and the oil are contacted in a counter-current extraction zone with refluxing.

10. A method as claimed in claim 2 in which the solvent and oil are contacted in a counter-current extraction zone and the solvent phase is heated to a higher temperature to precipitate a reflux phase.

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