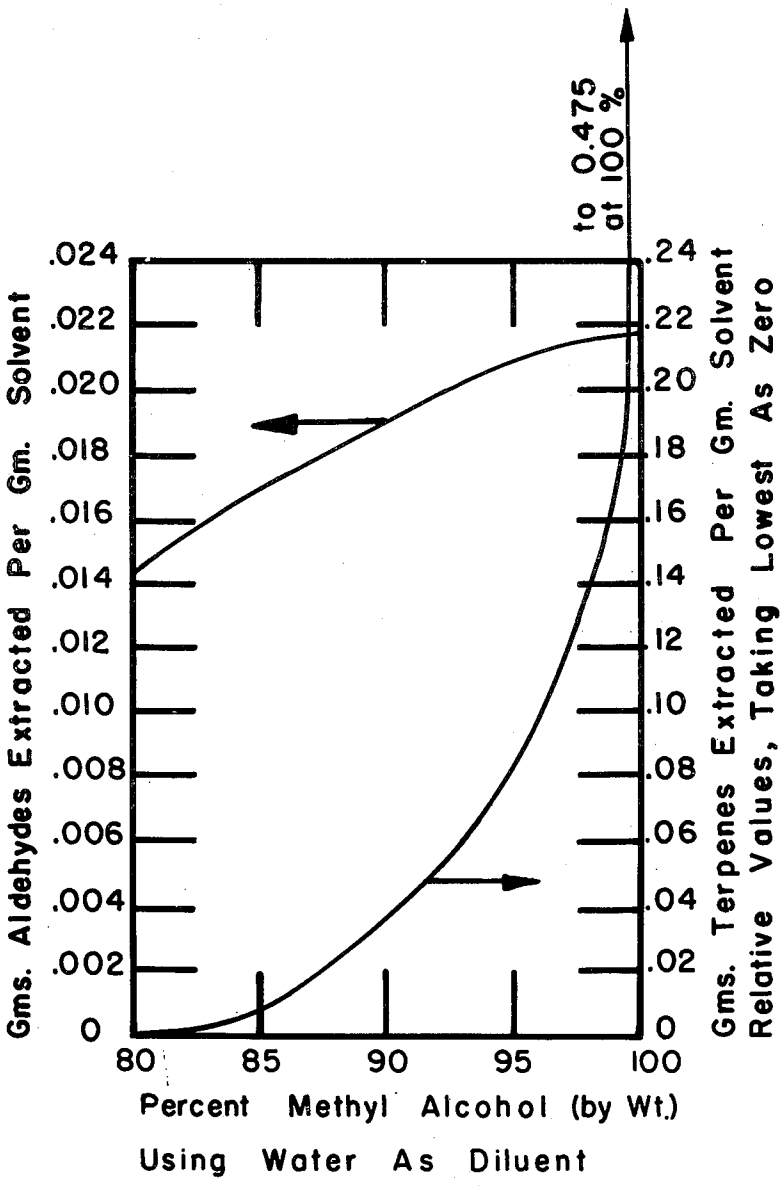
March 10, 1953 D. F. OTHMER ET AL 2,631,145

SEPARATION OF ESSENTIAL OILS INTO COMPONENT FRACTIONS

Filed April 10, 1951 3 Sheets-Sheet 1



DETERMINATION OF OPTIMUM METHYL ALCOHOL PERCENT TO BE USED FOR LEMON OIL EXTR'CT'N

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Fig. 1

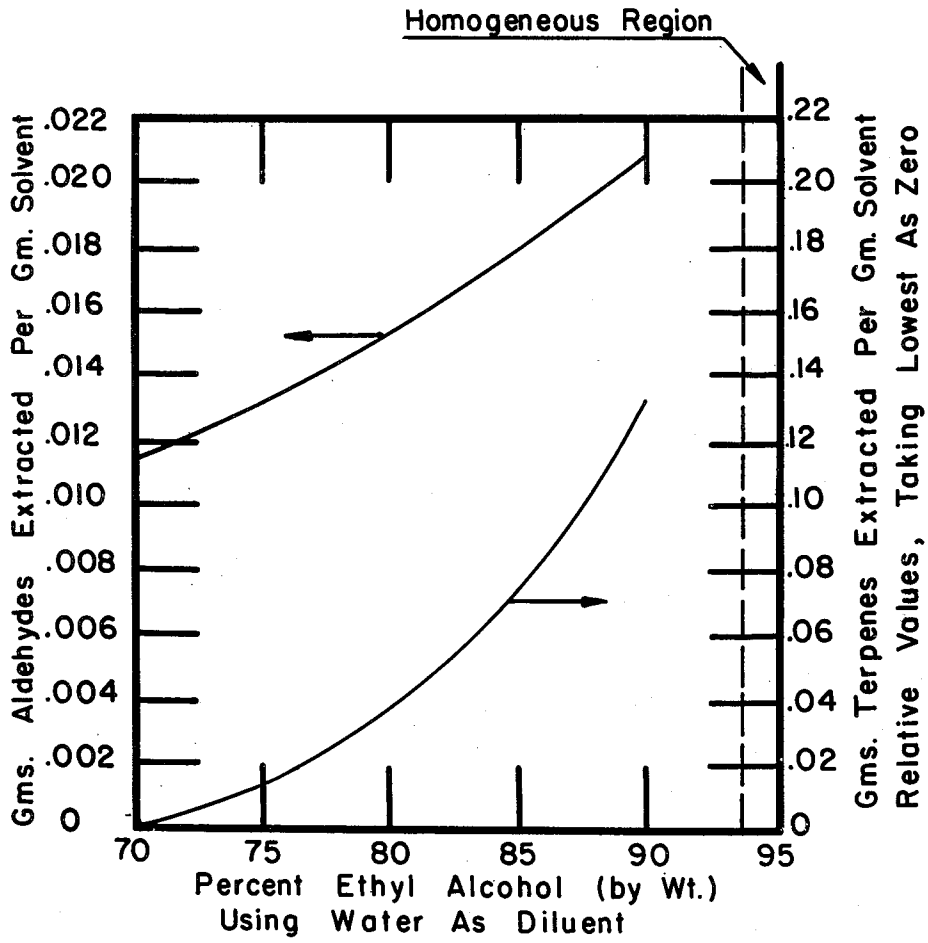

Fig. 2

DETERMINATION OF OPTIMUM ETHYL ALCOHOL PERCENT TO BE USED FOR LEMON OIL EXTR'CT'N

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SEPARATION OF ESSENTIAL OILS INTO COMPONENT FRACTIONS

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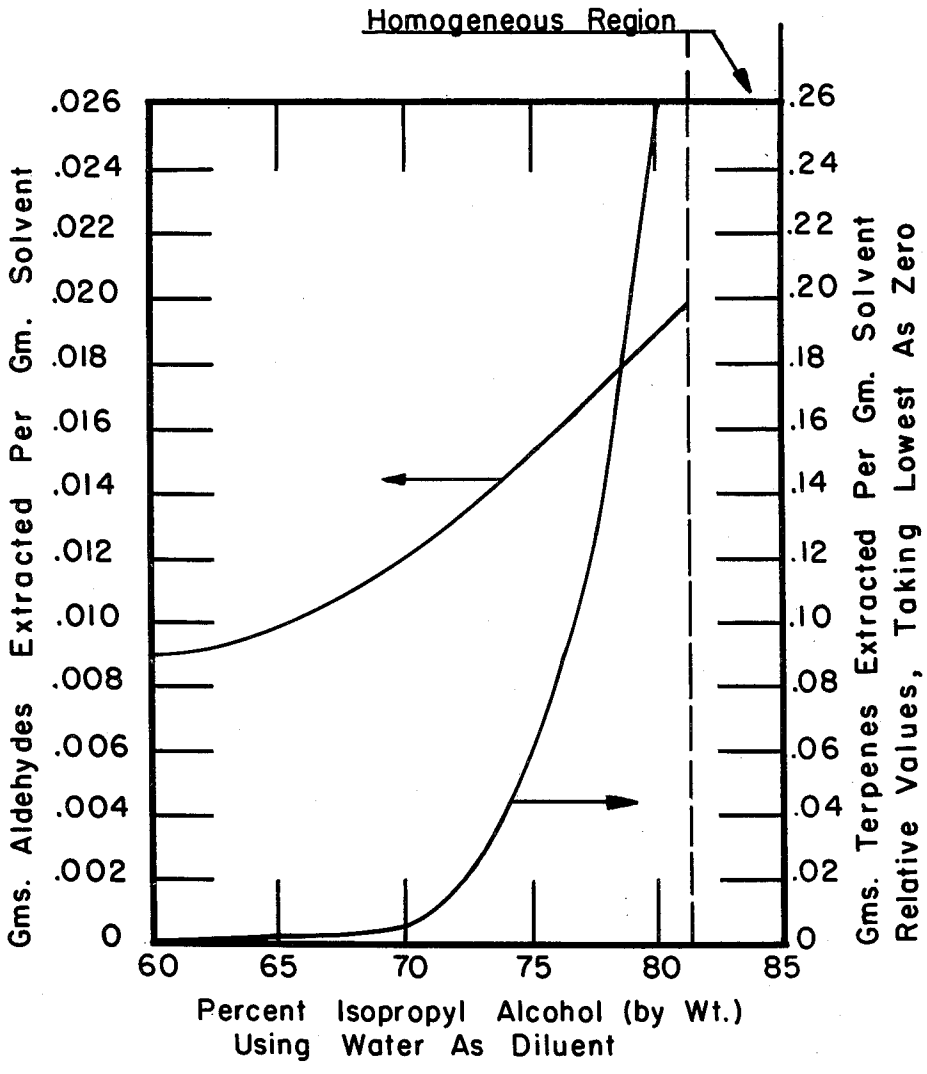

DETERMINATION OF OPTIMUM ISOPROPYL ALCOHOL PERCENT TO BE USED FOR LEMON OIL EXTR'CT'N

Fig. 3

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SEPARATION OF ESSENTIAL OILS INTO COMPONENT FRACTIONS

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8 Claims. (Cl. 260—236.6)

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This invention relates to a method of separation of essential oils into fractions, and more particularly it relates to a separation of essential oils into a fraction of highly concentrated or substantially pure hydrocarbon compounds and a fraction of highly concentrated or substantially pure oxygenated compounds.

Essential oils comprise a plurality of hydrocarbons, classified as terpenes and sesquiterpenes associated with oxygenated compounds, such as organic esters, alcohols, ketones, acids, aldehydes and the like. In the utilization of essential oils as flavoring agents the desirable fraction of the essential oil is the said oxygenated fraction, comprising a plurality of oxygenated compounds such as citral, geraniol, and the like.

The present commonly used commercial process for isolating the oxygenated fraction of essential oils comprises fractional distillation under vacuum to remove the hydrocarbon fraction consisting of the terpenes, followed by further distillation under vacuum to remove the desirable oxygenated compounds found in the essential oils, thereby leaving behind a residue in the distilling flask consisting of the higher boiling sesquiterpenes.

This commonly used fractional distillation process results in an essential oil oxygenated fraction having a "burnt taste," which is quite objectionable for many flavoring purposes.

A method of separating the essential oil oxygenated compounds, i. e., the compounds containing oxygen, found in essential oils, using aqueous alcohol without using relatively low temperatures, has been introduced by Van Wijk et al. and comprises the use of two solvents, one solvent being a non-polar hydrocarbon such as pentane, and the other solvent comprising a mixture of polar compounds such as aqueous methanol.

Application of this prior art of the Van Wijk et al. aqueous alcohol process produces obnoxious emulsions, and although use of 0.1 per cent of citric or tartaric acid is suggested as being helpful in alleviating emulsion formation in some instances, the problem of emulsion formation is nevertheless so serious as to render the process uneconomical or commercially inoperable.

This invention will be better understood by referring to the following figures forming a part

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of this disclosure and in which Fig. I is a graph showing the relationship between the amount of methanol in aqueous solution and the amount of aldehydes as representative of oxygenated components extracted from lemon oil by an aqueous methanol solution of that strength. The amount of undesirable terpenes, in relative values, extracted by each different composition of aqueous methanol is also shown.

Fig. II is an analogous graph using aqueous ethanol as the solvent, and Fig. III is another analogous graph using aqueous isopropyl alcohol as the solvent.

It is an object of this invention to separate the oxygenated compounds found in essential oils from the hydrocarbon compounds associated therewith by an economical process which is substantially free from emulsion formation.

It is also an object of this invention to produce an essential oil oxygenated fraction using but a single solvent which is adjusted in solvent extraction power through the addition of more or less water to an optimum value, which value enables the extraction of a maximum amount of desirable oxygenated components with a minimum amount of undesirable components.

It is also an object of this invention to produce an essential oil oxygenated fraction having substantially no "burnt taste."

Other objects will become apparent upon reading the following description of our invention.

According to our invention essential oil compositions are separated into two liquid phases by means of organic solvents which are more or less miscible with water and which contain more or less water, for example, (*a*) lower aliphatic alcohols such as methanol, ethanol, isopropanol and the like; (*b*) organic aliphatic acids such as formic acid, acetic acid, propionic acid; and like acids; and (*c*) ketones such as acetone, methylethyl ketone, diethyl ketone and the like. These solvents may all be mixed with more or less water to give an optimum concentration, critically adapted to dissolve preferentially the oxygenated fraction of essential oils, i. e., lemon oil, orange oil, peppermint oil, bay oil, spearmint oil, and the like, away from the hydrocarbon, i. e., terpene and sesquiterpene fraction. The said critically adapted aqueous organic solvent is added to the essential oil composition; and the resulting mix-

ture is agitated to effect intimate contact between the said critically adapted aqueous organic solvent and the essential oil composition; thereafter a separation gives two liquid phases, which in turn are easily separated by conventional procedures, using conventional apparatus, for example, by using separatory vessels, centrifuges, continuous liquid-liquid extractors, and like apparatus.

By the phrase "essential oil compositions" as used in this disclosure, we mean to include the oxygenated and hydrocarbon components of naturally occurring or semi-refined essential oil as well as these oils mixed with a non-polar or relatively non-polar liquid as, for example, cottonseed oil or other edible oils, or with non-polar hexane, pentane, and the like, as well as the admixture of these essential oils with a non-polar or relatively non-polar solid like hydrogenated fats and oils, and waxes or other relatively high-boiling non-polar materials which substances being non-polar liquids or solids facilitate the removal of the oxygenated components of the essential oil away from the terpenes and sesquiterpenes, by the said critically adapted aqueous organic solvent, alone or admixed with the above stated non-polar substances.

The addition of a non-polar substance which is miscible and compatible with terpenes and sesquiterpenes decreases the solubility of the aqueous solvent fraction and thus effects a sharp separation into a layer containing the desirable oxygenated compounds and a layer containing the undesirable hydrocarbon terpenes and sesquiterpenes.

By way of illustration, but not as a limitation of our invention, we employ an aqueous solution of methanol, ethanol, or isopropyl alcohol to effect the preferential solution of the oxygenated compounds away from the remainder of the essential oil, or from a mixture of the essential oil mixed with cottonseed oil, hexane, or other non-polar substance.

In general our method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbons of (*a*) essential oils and (*b*) essential oil compositions admixed with added non-polar substance comprises adding to the essential oil or essential oil composition an aqueous solution of a single organic solvent adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds in the manner described below, agitating the liquid mixture to effect intimate contact between the aqueous solvent and the essential oil composition so that the oxygenated compounds are dissolved in the aqueous solvent, separating the mixture into two substantially non-miscible layers, one of the said two layers consisting of the aqueous solvent containing the oxygenated compounds and the other layer consisting of the liquid hydrocarbon compounds and thereafter recovering the desirable oxygenated compounds from the aqueous solvent layer. The extraction may be conducted in one or several stages using fresh solvent in each stage or the same solvent counter-currently.

Different methods of obtaining the critically adapted aqueous solvent can be used, as for instance, by determining the cloud point by adding water to a solution of an essential oil composition dissolved in a solvent such as methanol, ethanol, isopropanol, acetic acid, and the like. However, our preferred method is that described in detail in the examples given hereinafter.

EXAMPLE I

Anhydrous methanol was diluted with water to produce alcoholic solutions containing 95, 90, 85, and 80 per cent methanol. These aqueous solutions, as well as 100 per cent methanol, were used to dissolve out the oxygenated compounds from lemon oil away from the terpenes and sesquiterpenes therein. The concentration of the extracted oxygenated compounds was determined by means of the aldehyde content found in the aqueous methanol extract after extraction of an essential oil therewith. The results are given in the Table I below.

Table I

EXTRACTION OF OXYGENATED COMPOUNDS FROM LEMON OIL BY MEANS OF AQUEOUS METHANOL OF VARIOUS CONCENTRATIONS

Solvent, percent methanol in water	100	95	90	85	80
Grams aldehyde originally present in 25 cc. of the lemon oil	1.15	1.15	1.15	1.15	1.15
Grams aldehyde extracted from the lemon oil per gram of solvent	0.0219	0.0212	0.019	0.017	0.0143
Grams terpenes and sesquiterpenes extracted per gram solvent (relative values)	0.475	0.085	0.042	0.002	0.000

(This relationship is shown in Fig. I.)

EXAMPLE II

By way of another embodiment, ethanol was diluted with water to produce solutions having concentrations of 90, 85, 80, 75, and 70 per cent ethanol. These aqueous ethanol solutions were used to dissolve the oxygenated compounds of lemon oil away from the hydrocarbon components associated therewith. The amount of extracted oxygenated compounds in the aqueous ethanol layer was determined by means of a standard test for aldehyde content. The results are given in Table II below.

Table II

EXTRACTION OF THE OXYGENATED COMPOUNDS FROM LEMON OIL BY MEANS OF AQUEOUS ETHANOL OF VARIOUS CONCENTRATIONS

Solvent, percent ethanol in water	90	85	80	75	70
Grams aldehyde originally present in 25 cc. of the lemon oil	0.89	0.89	0.89	0.89	0.89
Grams aldehyde extracted from the lemon oil per gram of solvent	0.0210	0.0176	0.0158	0.0133	0.0116
Grams terpenes and sesquiterpenes extracted per gram solvent (relative values)	0.132	0.082	0.0225	0.0143	0

(This relationship is shown in Fig. II.)

EXAMPLE III

As still another embodiment of our invention, isopropyl alcohol was diluted with water to yield alcoholic solutions of 80, 75, 70, 65 and 60 per cent isopropyl alcohol. These aqueous isopropyl alcohol solutions were used to dissolve out the oxygenated compounds from lemon oil. The quantity of oxygenated compounds extracted was determined by means of the aldehyde con-

tent of the aqueous isopropyl alcohol extract. The results are given in the Table III below.

Table III

EXTRACTION OF THE OXYGENATED COMPOUNDS FROM LEMON OIL BY MEANS OF AQUEOUS ISOPROPYL ALCOHOL OF VARIOUS CONCENTRATIONS

Solvent, percent isopropyl alcohol in water---	80	75	70	65	60
Grams aldehyde originally present in 25 cc. of the lemon oil---------	1.15	1.15	1.15	1.15	1.15
Grams aldehyde extracted from the lemon oil per gram of solvent----	0.0192	0.0158	0.0119	0.0100	0.0088
Grams terpenes and sesquiterpenes extracted per gram solvent (relative values)---------	0.261	0.0597	0.0039	0.0033	0

(This relationship is shown in Fig. III.)

The "relative values" of terpene solubility given in the tables above obtained by the residual weight method are converted to "absolute values" by means of the determination of the terpene solubility index which is equal to the value of the loss in weight of lemon oil during extraction minus the weight of total desirable components extracted from the lemon oil. The optimum solvent strength is then indicated as that strength at which the terpene solubility index is zero, which solvent strength is then used for the extraction of the specific essential oil. For lemon oil these values are 85 per cent aqueous methanol, 78 per cent aqueous ethanol, and 70 per cent aqueous isopropyl alcohol. Extracting 100 parts lemon oil with 100 parts of 85 per cent aqueous methanol using a countercurrent six-stage extraction battery followed by distilling the aqueous methanol extract under vacuum, keeping the temperature of the liquid below 80° C. in order to remove the aqueous methanol away from the desirable oxygenated components gave an excellent lemon oil concentrate having 48.4 per cent aldehyde content. This aldehyde content is equivalent to a concentration of aldehyde fifteen times that present in the original lemon oil.

By way of still another embodiment of our invention, 300 cc. volume of lemon oil containing 4.04 per cent aldehydes was mixed with 1.5 times its volume of cottonseed oil and there were added to this solution 4.8 volumes of isopropyl alcohol adjusted with water to optimum solvent strength by determining its cloud point. The temperature was raised to 80° C. to form a homogeneous mixture whereupon the temperature was lowered immediately in order to avoid thermal exposure. The resulting mixture was transferred to a separatory funnel and was then placed in a refrigerator and allowed to separate. The aqueous alcohol layer was removed and distilled under vacuum, yielding a concentrate which contained 14.7 per cent of aldehydes, a concentration 3.64 times that present in the original essential oil. On a volume basis, this is equivalent to an aldehyde concentration of about 6 times that found in essential oil. A second extraction of the essential oil in the same way yielded an additional 7.1 per cent of aldehydes. Concentration of all of the extracts obtained yielded a concentrate containing about 25 per cent of aldehydes, representing nearly a six-fold concentration of aldehydes over that present in the original lemon oil. The quality of the products obtained were excellent by organoleptic tests.

For simplicity it is usually preferred to use a solvent comprising only one water soluble solvent and water with either the essential oil or the essential oil composition (including oils, hydrocarbons or like non-polar liquids). In some cases we have found that two or more alcohols to which water is added or two or more ketones, acids, etc. to which water is added may give a sharper separation. We have also found that mixtures of two or more materials selected from the several chemical classes (e. g., methanol, ethanol, and acetone) may be especially advantageous for our process under some conditions.

Thus, our invention produces a fraction of terpene-free or substantially terpene-free oxygenated compounds, according to the concentration of the solvent employed, which fraction has substantially no "burnt taste" and is superior in other qualities to that obtainable by the present commonly used method mentioned above. The oxygenated essential oil compounds of our invention may be separated from the aqueous solvent by dilution with water, or by distillation, under vacuum conditions, of the aqueous solvent away from the oxygenated extract at temperatures less than 80° C., thereby avoiding a "burnt taste" and yielding a superior solvent-free fraction for commercial use.

The product obtained by dilution with water of the aqueous solvent extract may be improved in quality if desired by a relatively short steam distillation treatment, preferably under vacuum. We have found that the essential oil oxygenated components obtained by distillation under vacuum of our aqueous solvent as well as oxygenated components obtained by a shortened steam distillation of a diluted extract give a fraction of oxygenated components superior to those currently commercially available.

The terpene fraction obtained by using the process of our invention is also a saleable product since it is substantially free from oxygen containing compounds.

We have also found that other methods of separating the aqueous organic solvent from the oxygenated compounds dissolved therein may be used besides those of distillation under vacuum and of dilution with water mentioned above. These have included cryoscopic procedures whereby the use of freezing temperatures are employed to separate the molecules into a solid phase and a liquid phase, or into two liquid phases, one of which is enriched with the desired oxygenated components; also we may use salting-out procedures for separating out the desirable dissolved oxygenated components from the aqueous solvent, as well as other procedures.

The recovery of the aldehydes in the original essential oil may be as high as 90 to 95 per cent depending upon the number or multiplicity of extraction stages employed, or upon the height of the extraction column used in the extraction of the essential oil with the aqueous solvent, or upon the ratio of oil or other non-polar liquid used in the essential oil composition, or upon the difference of temperature employed between the upper or homogenizing temperature and the lower or decanting temperature.

It is therefore the purpose of this invention to extract the oxygenated compounds from either an essential oil or from an essential oil composition, viz. essential oil diluted with, for example, an edible oil such as cottonseed oil or diluted with non-polar hydrocarbons such as hexane and the like. Extraction of the oxygenated compounds from an essential oil composition containing non-polar additives has an advantage in that terpene

and sesquiterpene hydrocarbons are soluble in the non-polar solvent and thereby effect a sharp separation of the aqueous solvent layer from the hydrocarbon layer on freezing or on applying other conventional separation procedures.

This invention is illustrated by way of several embodiments, but it is not to be limited to these embodiments, since it is of broader scope.

We claim:

1. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in essential oils consisting of adding to an essential oil an aqueous solution of an organic solvent adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the essential oil; agitating the liquid mixture to effect intimate contact between the aqueous solvent and the essential oil whereby the oxygenated compounds are dissolved in the aqueous solvent; separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous solvent containing the oxygenated compounds and the other layer consisting of the liquid hydrocarbon compounds and thereafter recovering the oxygenated compounds from the aqueous solvent layer.

2. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in essential oils consisting of adding to an essential oil an aqueous solution of an organic solvent adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the essential oil; agitating the liquid mixture to effect intimate contact between the aqueous solvent and the essential oil whereby the oxygenated compounds are dissolved in the aqueous solvent; separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous solvent containing the oxygenated compounds and the other layer consisting of the liquid hydrocarbon compounds and thereafter recovering the oxygenated compounds from the aqueous solvent layer at a temperature of less than 80° C. to obtain the oxygenated components free from a "burnt taste."

3. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in essential oils consisting of adding to an essential oil an organic solvent, adjusting the said organic solvent with water to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrcarbon compounds present in the said essential oil, raising the temperature to effect a homogeneous solution of all components, then lowering the temperature to separate the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous solvent containing the dissolved oxygenated compounds and the other layer consisting of the liquid hydrocarbon compounds and the relatively non-polar components, and thereafter recovering the oxygenated compounds from the aqueous solvent layer.

4. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in essential oils consisting of adding to an essential oil an organic solvent adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the essential oil, raising the temperature to effect a homogeneous solution of all components, then lowering the temperature to obtain two phases thereby separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous solvent containing the dissolved oxygenated compounds and the other layer consisting of the liquid hydrocarbon compounds and the relatively non-polar components, and thereafter recovering the oxygenated compounds from the aqueous solvent layer.

5. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in lemon oil consisting of adding to the lemon oil an aqueous solution of an organic solvent adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the lemon oil; agitating the liquid mixture to effect intimate contact between the aqueous solvent and the lemon oil whereby the oxygenated compounds are dissolved in the aqueous solvent, separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous solvent containing the oxygenated compounds and the other layer consisting of the lemon oil hydrocarbon compounds; and thereafter recovering the oxygenated compounds from the aqueous solvent layer.

6. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in lemon oil consisting of adding to the lemon oil an aqueous solution of an organic solvent adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the lemon oil; agitating the liquid mixture to effect intimate contact between the aqueous solvent and the lemon oil whereby the oxygenated compounds are dissolved in the aqueous solvent separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous solvent containing the oxygenated compounds and the other layer consisting of the lemon oil hydrocarbon compounds; and thereafter recovering the oxygenated compounds from the aqueous solvent layer at a temperature of less than 80° C. to obtain the oxygenated components free from a "burnt taste."

7. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in lemon oil consisting of adding to the lemon oil an aqueous solution of methyl alcohol adjusted in solvent strength to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the lemon oil; agitating the liquid mixture to effect intimate contact between the aqueous solvent and the lemon oil whereby the oxygenated compounds are dissolved in the aqueous methanol; separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous methanol containing the oxygenated compounds and the other layer consisting of the lemon oil hydrocarbon compounds and thereafter recovering the oxygenated compounds from the aqueous solvent layer.

8. The method of separating the oxygenated compounds from the terpene and sesquiterpene hydrocarbon compounds found in lemon oil consisting of adding to the lemon oil an aqueous

solution of methyl alcohol adjusted to 85 percent concentration to obtain maximum solubility of the oxygenated compounds and minimum solubility of the hydrocarbon compounds present in the lemon oil; agitating the liquid mixture to effect intimate contact between the aqueous solvent and the lemon oil whereby the oxygenated compounds are dissolved in the aqueous methanol; separating the mixture into two substantially non-miscible layers, one of said two layers consisting of the aqueous methanol containing the oxygenated compounds and the other layer consisting of the lemon oil hydrocarbon compounds; and thereafter recovering the oxygenated compounds from the aqueous solvent layer.

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