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SEPARATING FATTY ACIDS

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This invention relates to the separation of fatty acids from mixtures of fatty acids obtained from natural or synthetic sources, and it comprises processes wherein the fatty acids in said mixture are converted to nitriles, the mixture of nitriles separated by fractional distillation, and the separated nitriles converted to the corresponding fatty acids.

The separation of individual fatty acids from mixtures of fatty acids such as those obtained from the splitting or hydrolysis of coconut oil and other vegetable, animal and marine oils and fats is a problem of increasing importance. Many uses have been developed for substantially pure fatty acids. For example, pure dodecyl alcohol can be made from lauric acid. Lauric acid is a common constituent in coconut oil, in which it is combined with glycerine as a triglyceride. The pure fatty acids are also useful as starting materials for various synthetic reactions; and at the present time there is a substantial demand for the pure acids at prices greatly in excess of those paid for mixtures containing a plurality of the fatty acids.

Common sources of the fatty acids are the various triglycerides occurring in nature. Most of these triglycerides are mixtures of various triglycerides such as tristearin, trilaurin and others. Pure individual triglycerides practically never occur. For example, butter fat will contain triglycerides of butyric, caproic, caprylic, capric, lauric, myristic, palmitic, and stearic acids. The usual method of preparing pure fatty acids from such a starting material consists in splitting the fat to obtain glycerine and a mixture of fatty acids. These fatty acids are then separated by distillation at high vacuum to obtain rough fractions which are then redistilled under vacuum to obtain closer cuts. Vacuum distillation is necessary since the free fatty acids, especially those containing twelve or more carbon atoms, cannot be distilled at atmospheric pressure without undergoing decomposition. Vacuum distillation, however, is disadvanageous because it lessens the difference in boiling point between any two acids. In other words a sharp separation or cut is difficult to obtain. Moreover, constant boiling mixtures are often encountered and these cannot be separated by ordinary fractional distillation. Even under a high vacuum, many of the fatty acids such as palmitic and stearic decompose somewhat. In general it can be said that the preparation of pure fatty acids by distillation of a mixture of fatty acids is essentially impossible in practice if the mixtures are at all complex.

In the past it has been suggested to convert mixtures of fatty acids to their corresponding simple aliphatic esters such as the ethyl esters and then fractionate the esters. Although the simple alkyl esters are somewhat more stable than the acids, the higher members of the series must be distilled under a vacuum to avoid decomposition. Constant boiling mixtures, requiring numerous redistillations, are commonly encountered, and the problem of isolating pure fatty acids from mixtures has been exceedingly difficult.

We have now discovered a simple and effective way of separating or isolating fatty acids from naturally occurring or synthetic mixtures of a plurality of fatty acids. We have discovered that the nitriles of these fatty acids can be fractionally distilled at atmospheric pressure without encountering any decomposition and with very little tendency for the formation of constant boiling mixtures. Having thus obtained substantially pure nitriles of the fatty acids, we can then hydrolyze these nitriles to convert them to the fatty acid. Or we can convert the pure nitriles to soaps of the fatty acid by treatment of the nitrile with alkali solutions. Then, if desired, these soaps can be converted to the free fatty acid.

In broad aspects our invention is based upon the discovery that a mixture containing a plurality of fatty acids can be subjected to the action of ammonia at elevated temperatures in the presence of a dehydrating catalyst to convert the fatty acids in said mixture to their corresponding nitriles, that the resulting mixture of fatty acid nitriles can be fractionally distilled at atmospheric pressures to get, in a single distillation, fractions which are composed of substantially pure individual nitriles, and that these nitriles can then be converted back to their corresponding fatty acids. Thus, in our invention, we are converting the mixture of fatty acids to a mixture of nitriles corresponding to the fatty acids; we are separating these nitriles by fractional distillation; and we are reforming the fatty acids from the distilled fractions. We are, in effect, separating the fatty acids by the expedient of converting them to their nitriles.

We shall now describe our invention with specific reference to the separation of pure fatty acids obtained from coconut oils.

When coconut oil is split or hydrolyzed, there is obtained a mixture of fatty acids containing varying quantities of caproic, caprylic, capric, lauric, myristic, palmitic and stearic acids In coconut oil the fatty acids are chiefly lauric and myristic,

together with smaller amounts of palmitic and stearic, and much less quantities of the other acids noted above.

In the practice of our invention we convert this crude mixture of some seven fatty acids to their corresponding nitriles by passing the mixture in the vapor phase together with ammonia gas over a dehydrating catalyst, such as aluminum oxide, at a temperature of about 375° C., and condense the reaction products. Practically no decomposition of the free fatty acid occurs because the vapors are diluted with ammonia and the ammonia seems to have some protective influence against decomposition. In the presence of the catalyst the ammonia converts the free fatty acids to nitriles and the mixture of nitriles thus obtained is condensed. Various well-known dehydrating catalysts of the metal oxide type can be used instead of aluminum oxide but aluminum oxide is most convenient. It can be precipitated on pumice or other inert carriers if desired. Ways of converting a fatty acid to its corresponding nitrile are a part of the prior art, although we are not aware that others have deliberately started with a mixture of various fatty acids and converted said mixture to a mixture of nitriles. Thus, for example, the nitriles can be prepared by the dry distillation of ammonium salts of the fatty acids in the presence of phosphorous pentoxide or other dehydrating agent. Quite possibly when ammonia gas is reacted with the free fatty acids in the presence of aluminum oxide, as described above, the first step in the process is the formation of ammonium soaps, the second is the decomposition of the soap to the corresponding acid amide, and finally further dehydration of the amide to the nitrile. We make no claim to any novelty in the methods of converting the fatty acids to their corresponding nitriles except that, as stated, we are not aware that others have ever deliberately started with a mixture of fatty acids.

Having converted the mixture of fatty acids to a mixture of fatty acid nitriles we then fractionally distil the nitrile mixture at atmospheric pressure. We can, of course, distil under a slight vacuum if desired or even under an elevated pressure, but neither of these expedients are of any pronounced advantage. In the following table we have tabulated the results obtained when distilling a mixture composed of one thousand parts by volume of a mixture of nitriles obtained from coconut fatty acids.

Fraction	Volume	Boiling point ° C.	Nitrile in fraction
1	5	162-164	Capro
2	10	164-194	Capro and caprylo
3	60	194-198	Caprylo
4	25	198-235	Caprylo and capri
5	45	235-240	Capri
6	35	240-278	Capri and lauro
7	405	278-283	Lauro
8	35	283-308	Lauro and myristo
9	140	308-312	Myristo
10	80	312-338	Myristo and palmito
11	85	338-356	Palmito and stearo
12	80	356-362	Stearo
Residue	25		

It will be noted that the first fraction is substantially pure capronitrile, the third is substantially pure caprylo, the fifth is substantially pure caprinitrile and so on. Fractions 2, 4, 6, 8 and 10, which contain two different nitriles, such as capro and caprylonitrile can be refractionated. The marked sharpness of the cuts or fractions obtained is worthy of note. To our knowledge this is the first time that anyone has ever been able to separate fatty acid compounds by ordinary fractional distillation at atmospheric pressure to such a high degree as that indicated in the table. This is particularly noticeable in the case of capronitrile. The quantity of capronitrile in the distillation mixture is about five parts in one thousand. Yet no difficulty is encountered in recovering substantially pure capronitrile from the large volume of material distilled.

The individual fractions of nitriles are then converted to free fatty acids. We can do this in two ways. Generally we simply hydrolyze the nitrile, such as myristonitrile with a mineral acid such as hydrochloric or sulfuric. For example, one volume of the nitrile is refluxed for about two hours with a sulfuric acid solution consisting of three volumes of sulfuric acid and two volumes of water. The strength of the acid can vary over wide limits. When the hydrolysis is complete the free fatty acid, being insoluble in the aqueous sulfuric acid solution, can be separated by stratification, washed with water to remove any traces of acid, and dried. Thus from such a crude mixture as the fatty acids of coconut oil we can obtain pure caproic acid as well as various other acids found in such a raw material.

As an alternative method, we can hydrolyze the nitrile by heating it for three hours at a temperature of about 110° C. at two atmospheres pressure with an alcoholic caustic soda solution containing about 12 percent of caustic soda. This converts the nitriles to soaps of the fatty acids which can then be recovered from the reaction mixture in ways well known.

We can illustrate the effectiveness of our way of separating a mixture of free fatty acids into its components by first preparing a mixture containing definite known quantities of fatty acids, converting the mixture to nitriles, fractionating, distilling the nitriles, and then hydrolyzing the distillates. For example, we prepare a mixture containing equal parts of caproic, caprylic, and capric acids. This mixture is converted to the corresponding nitriles by treatment with ammonia in the presence of a dehydrating catalyst as described above. One thousand parts of these mixed nitriles are distilled and the following fractions obtained.

Fraction	Volume	Boiling point ° C.	Nitrile in fraction
1	315	164-168	Capro
2	35	168-194	Capro and caprylo
3	300	194-198	Caprylo
4	25	198-234	Caprylo and capri
5	300	234-237	Capri
Residue	25		

It will be noted from the above tabulated data that a particularly sharp separation can be obtained. The initial mixture of nitriles contains about 330 parts of capronitrile. On fractional distillation at atmospheric pressure fraction 1 consists of 315 parts of substantially pure capronitrile. Fractions 2 and 4 can, of course, be redistilled if desired.

In another illustration of our invention we prepare a mixture of fatty acid nitriles from a mixture of fatty acids obtained by splitting butter fat. One thousand parts of the mixture of nitriles is fractionally distilled at atmospheric pressure

and the following table indicates the fractions obtained.

Fraction	Volume	Boiling point ° C.	Nitrile in fraction
1	50	118–124	Butyro
2	5	124–158	Butyro and capro
3	15	158–166	Capro
4	25	166–281	Capro, caprylo, capri and lauro
5	15	281–284	Lauro
6	15	284–306	Lauro and myristo
7	35	306–315	Myristo
8	30	315–339	Myristo and palmito
9	385	339–344	Palmito
10	50	344–358	Palmito and stearo
11	260	358–363	Stearo
Residue	115	----------	----------

Butter fat consists primarily of triglycerides derived from butyric, palmitic, and stearic acids. It is to be noted that most all of these acids (as nitriles) were separated by fractional distillation in substantially pure condition.

Of course the nitriles in the various fractions indicated above can be hydrolyzed or converted to the free fatty acids as we have described.

In the commercial practice of our invention we find it advantageous to fractionally distil to get a plurality of fractions many of which consist of substantially pure nitriles, such as fractions 1, 3, 5, 7, 9 and 11 indicated above in connection with butter fat and other fractions containing a plurality of nitriles but in very small quantities such as fractions 2, 4, 6, 8 and 10 above. These fractions containing two or more nitriles can then be mixed together and added to further quantities of a fresh mixture of nitriles to be fractionally distilled. This is somewhat more convenient than redistilling fractions 2 and 4, for example, which contain relatively small quantities of nitriles. Although we have described our invention with especial reference to separating fatty acids from coconut oil and butter fat it is to be understood that the methods described above are applicable to the separation of any mixture of fatty acids containing two or more fatty acids.

We need not always hydrolyze the separated nitriles. These nitriles are starting materials for many organic syntheses and our invention provides a process whereby the substantially pure, individual nitriles can be obtained from such crude mixtures as coconut fatty acids. We are not aware that anyone has hitherto prepared fatty acid nitriles from such crude sources and our invention broadly includes the conversion of the crude mixture of acids to a crude mixture of nitriles and then fractional distillation of the nitrile mixture.

Having thus described our invention what we claim is:

1. The process which includes converting a mixture of a plurality of fatty acids to a mixture of nitriles corresponding to said fatty acids, separating the nitriles by fractional distillation, and converting the separated nitriles to their corresponding fatty acids.

2. The process which includes converting a mixture of a plurality of fatty acids to a mixture of nitriles corresponding to said fatty acids, separating the nitriles by fractional distillation, and hydrolyzing the separated nitriles to convert them to their corresponding fatty acids.

3. The process which includes treating a vaporized mixture of a plurality of fatty acids with ammonia in the presence of a dehydrating catalyst at an elevated temperature to convert the fatty acids to a mixture of nitriles corresponding to said fatty acids, separating the nitriles by fractional distillation and hydrolyzing the separated nitriles to convert them to their corresponding fatty acids.

4. The process as in claim 2 wherein the nitriles are hydrolyzed with a mineral acid.

5. The process as in claim 2 wherein the nitriles are hydrolyzed with an alkali solution.

6. The process as in claim 3 wherein the nitriles are hydrolyzed with a mineral acid.

7. The process as in claim 3 wherein the nitriles are hydrolyzed with an alkali solution.

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