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PREPARING FATTY ACID COMPOUNDS

John Ross, New York, N. Y., and Hans George Kirschenbauer, Ridgefield, N. J., assignors to Colgate-Palmolive-Peet Company, Jersey City, N. J., a corporation of Delaware

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This invention relates to the concentration of certain individual organic acids occurring in various mixtures of such acids and to the controlled halogenation of individual carboxylic acids.

It is often desirable to obtain relatively pure fatty acids or their derivatives for specific purposes, but it is generally a difficult task to procure such materials directly, since fatty acids usually occur in complex mixtures of their glycerides in oils or fats. The boiling points, melting points, solubilities, and other physical properties of the fatty acids in these mixtures are such that they do not readily permit direct separation of one acid from another.

Furthermore, it is often necessary to use the mono-halogenated derivatives of these fatty acids, for example, in the preparation of mono-olefinic unsaturated fatty acids by a method described in the copending application Serial No. 267,608, filed April 13, 1939. It has been found, however, that if a mixture of fatty acids, such as is normally obtained from fatty oils, is chlorinated to the proper chlorine percentage corresponding to completely monochlorinated fatty acids, actually a mixture of polychlorinated fatty acids, monochlorinated fatty acids, and non-chlorinated fatty acids results. Such a mixture is unsuitable for many purposes where a relatively uniform product is required. For example, if a mixture of this type is treated in the process of the copending application Serial No. 267,608, filed April 13, 1939, a mixture containing saturated fatty acids, mono-olefinic fatty acids, and polyolefinic fatty acids would be obtained.

It has now been found that the reactivity with halogens of the different fatty acids varies greatly, depending on the stereo-chemical structure of the acid. It has been further discovered that between two or more aliphatic acids under the same or equivalent conditions, the more reactive aliphatic acid after monohalogenation is often still relatively more reactive than the other non-halogenated acid or acids, and will tend to be poly-halogenated before the less reactive non-halogenated acid or acids will be monohalogenated. For example, in a mixture of stearic and palmitic acids, chlorine will substitute the palmitic acid first to produce monochloropalmitic acid, and leave substantially non-chlorinated stearic acid. Upon further chlorination, the monochloropalmitic acid will be largely converted to dichloropalmitic acid and leave the major portion of the stearic acid non-halogenated. The formation of uniformly monochlorinated, high molecular weight long-chain fatty acids in such a mixture is not a simple problem.

It has also been found that the monohalogenated acids are very different in their physical properties from the non-halogenated fatty acids, thus affording means for the separation of the individual acids.

By the process of the present invention, it is possible to prepare uniformly halogenated fractions of fatty acids. It is also possible to prepare relatively pure aliphatic carboxylic acids, and halogenated aliphatic carboxylic acids from complex mixtures of aliphatic carboxylic acids.

The process of this invention comprises the direct halogenation of a mixture of aliphatic carboxylic acids until the most reactive acid is monohalogenated. This halogen-containing acid is then separated from the non-halogenated, less-reactive acids by any suitable means, such as by fractional crystallization from organic solvents. The remaining unreacted acid may then again be treated with halogen to produce the monohalogen derivative of the aliphatic acid of next order of reactivity. This monohalogenated acid is removed and the above procedure repeated to the desired degree of separation. The individual fractions may then be recombined to obtain a mixture of uniformly monohalogenated fatty acids, or they may be used in their relatively pure state for specific purposes.

It is clear that this procedure may be utilized to prepare a monohalogen acid of one chemical individual which can be separated from another non-halogenated fatty acid, thus obtaining the latter in a substantially pure state as a chemical individual. For example, pure stearic acid may be obtained from a triple-pressed stearic acid containing about equal parts of palmitic and stearic acids by separation of monochloropalmitic acid from the unreacted stearic acid, according to the procedure described in Example I.

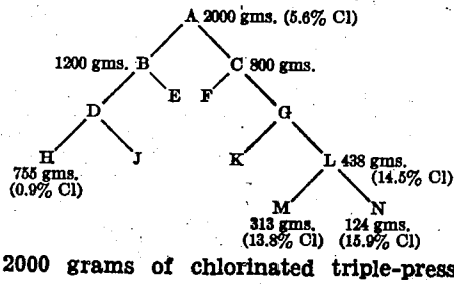
The degree of halogenation of the individual acids in each of the process steps need not be monohalogenation as indicated above, but may

be di- or polyhalogenation with the same or different halogens. However, it is preferred to monohalogenate in this treatment, since monohalogenated acids are the most difficult, or even impossible, to prepare from mixed fatty acids by any means heretofore described, and by this procedure the individual acids are most readily separated. The individual products in the monohalogenated state can then be further halogenated with the same or different halogens if desired.

For the purpose of giving a better understanding of the present invention, but in no way limiting the scope thereof, the following examples are given:

Example I

2000 grams of triple-pressed commercial stearic acid, titer 55.7° C., were melted and chlorine gas bubbled into the liquid acid until the gain in weight at this temperature was equal to 128 grams. The product was washed with water and dried. It was found to contain 5.6% chlorine by weight. Fractional crystallization of this material from acetone solution gave the following yields of acids which contained the percentage of chlorine indicated in the following chart.

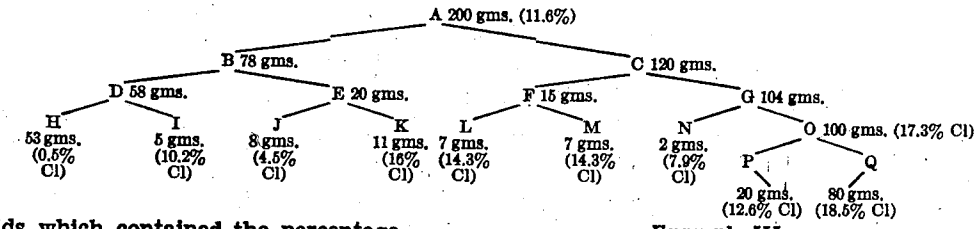


The 2000 grams of chlorinated triple-pressed stearic acid (A) (Cl=5.6%) were dissolved in an equal weight of warm acetone, and upon cooling to 0° C., 1200 grams of solid crystalline acid (B) was deposited and subsequently filtered off from the mother liquor which contains a mixture of acids designated as (C). This solid acid B was redissolved in fresh acetone and crystallized to give solid acid D, and the acid in this mother liquor is designated as E. The solid acid D was recrystallized from acetone and gave 755 grams of the fraction H, which was substantially pure stearic acid (acid value 201.1, equivalent or molecular weight 279 and a titer point of 64.1° C.). Pure stearic acid has acid value 197.3, equivalent or molecular weight 284.4, and titer point of 69 to 71° C.

The mother liquor C was successively concentrated and cooled, and in turn deposited in solid acids F, K and M. The final mother liquor N was mainly monochloropalmitic acid containing some admixed dichloro-acid. Fraction M, possessing an acid value of 187.1, equivalent or molecular weight 299.8, is essentially pure monochloropalmitic acid (acid value 192.9, equivalent or molecular weight 290.8).

Example II

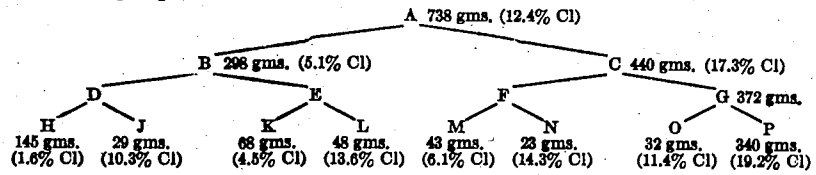
200 grams triple-pressed stearic acid were chlorinated at a temperature of 90° C. until the gain in weight was equal to 27 grams chlorine. The product was washed with water and dried, and was found to have a chlorine content of 11.6%. Recrystallization from acetone gave 53 grams of substantially pure stearic acid and 80 grams of dichloropalmitic acid (acid value 177.3, equivalent or molecular weight 316.4). Theory requires acid value 172.5, equivalent or molecular weight 325.3.



Example III

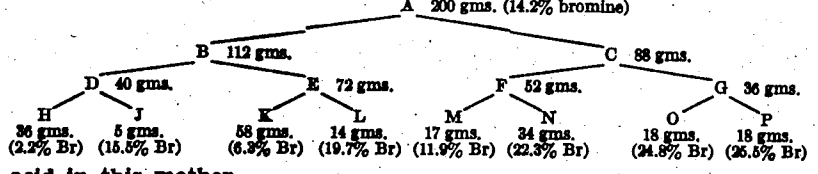
738 grams of stearic acid (Cl content 0.9%) purified as described in Example I were treated with chlorine at 90° C. until the gain in weight was 107 grams. The product was washed with water and dried. Analysis showed the product to have a chlorine content of 12.4%. Recrystallization from acetone showed that the product consisted of approximately 20% unchanged stearic acid, 20% monochlorostearic acid, and 50% dichlorostearic acid.

Fractional crystallization of chlorinated stearic acid:



Example IV

264 grams of triple-pressed stearic acid were brominated by the Hell-Volhardt-Zelinsky method until the bromine content was 14.2%. The product was washed and dried, and was then submitted to fractional crystallization from acetone according to the following scheme:



Fraction H possesses a titer point of 64.8° C., an acid value of 196.3, and an equivalent or molecular weight of 285.8. (The theoretical figures for pure stearic acid are: Acid value 197.3, equivalent or molecular weight 284.4.) The fractions O and

P, containing approximately 25% bromine, essentially consist of monobromopalmitic acid.

The above examples illustrate the chief features and advantages of the present invention, but are not limiting on the scope thereof. Although chlorinated acids are preferred for convenience and economical purposes, the corresponding brominated and/or other halogenated derivatives can be similarly prepared by treatment with bromine, iodine chloride, and the like. Solvents may also be present during the halogenation treatment, such as carbon tetrachloride, other halogenated hydrocarbons, acetic acid, and the like.

The solubilities of the sodium salts of chlorinated fatty acids in water at 28° C. are as follows:

	Liquid at the following limiting high concentrations
Triple-pressed stearic acid sodium soap per cent	0.25
Chlorinated triple-pressed stearic acid sodium soap. Chlorine content 5.9% per cent	0.4
Chlorinated triple-pressed stearic acid sodium soap. Chlorine content 10.1% per cent	1.0
Chlorinated triple-pressed stearic acid sodium soap. Chlorine content 21.4% per cent	13
Chlorinated triple-pressed stearic acid sodium soap. Chlorine content 25.1% per cent	20
Chlorinated triple-pressed stearic acid sodium soap. Chlorine content 27.4% per cent	23
Palmitic acid sodium soap ---------do----	0.3
Chlorinated palmitic acid sodium soap. Chlorine content 13.8% ------per cent	12.2

The solubility tests were carried out by preparing successive dilutions until the concentrations were just low enough so that the solutions on cooling to 28° C. would be liquids and would not assume a pasty or solid character. On direct halogenation of fatty acids, it is known that the action first takes place on the alpha carbon atom of the fatty acid, but, as indicated hereinbefore, applicants are the first to control the halogenation to form alpha monohalogenated higher fatty acids from the normally-occurring mixtures of these acids. This is true of other salts of these acids as well as their solubilities in organic solvents.

Normal fatty acids are the substances which generally occur in mixtures and to which the present invention is particularly adapted. However, it is also possible to apply the process to straight or branched chain saturated aliphatic mono- and poly-basic carboxylic acids. The process likewise may be applied to other derivatives of the acids, such as chain substituted acids including hydroxy, acyl, alkoxy, and acyloxy substituted acids of the above class, as well as carboxyl group functional derivatives of any of these acids, for example, acid halides, monohydric alcohol esters, and polyhydric alcohol full and partial esters.

The rate of halogenation of a given fatty acid is a function of the temperature at which the halogenation is carried out, the nature and intensity of the photocatalytic light radiation to which the acid is exposed, the concentration of the acid in solution, the nature of the solvent, and to a minor degree the presence of so-called halogenation catalysts such as halogen derivatives of phosphorus, sulphur, antimony, and other elements.

When all contributive and catalytic influences are equal, that is, under equivalent conditions of temperature, intensity, and type of light radiation, and concentration in the given solvent, we have found that the rate of halogenation of a given acid, and therefore the course of halogenation of a mixture of fatty acids, depends to a hitherto unsuspected degree upon the stereochemical structure of the acid.

The relative rate of halogenation (relative reactivity) in the even carbon chain fatty acids is a function of the number of carbon atoms. As one proceeds from short-chain fatty acids to long-chain fatty acids, the reactivity alternates, and it can be considered to be connected with the hypothetical helical structure which is a possible configuration for any given straight-chain fatty acid to assume in the molten or dissolved state.

In the case of chlorination, under equivalent conditions of temperature and light radiation, the relative rate of monochlorination of straight-chain fatty acids having an even number of carbon atoms has been found to be as follows: Palmitic acid>capric acid>lauric acid>caprylic acid>stearic acid>myristic acid.

Since each acid has its own specific rate of reaction with a halogen, as shown by the above table, for fatty acids reacting with a single chlorine, it is possible by the method of this invention to mono- or di-halogenate one or more acids in a mixture thereof and to separate the individual halogenated and non-halogenated acids by any convenient or desirable procedure.

The products of the process of this invention are particularly desirable for preparation of unsaturated fatty acids by the method described in the copending application Serial No. 267,608. They may be converted to the corresponding hydroxy carboxylic acid. Suitable derivatives, such as the salts of the acids, may be reacted at the halogen substituents with other substances, such as alcoholates and thioalcoholates to form ethers, salts to form esters, ammonia and amines to form amines or ammonium compounds. For example, they can be reacted with sodium sulphite to prepare sulphonated derivatives thereof, with or without remaining halogen and/or hydroxy groups. They may be reacted with sodium or potassium cyanide to form acid nitriles which may be hydrolyzed to yield polybasic carboxylic acids useful in the preparation of plastics by reaction with polyamines or polyhydric alcohols. They can be condensed with aromatic or sulphonated aromatic nuclei by the Friedel-Crafts synthesis. The various derivatives such as glycerides and other esters, acid halides, ketones, soaps, and related substances can be prepared from the halogenated fatty acids, or in some cases they can be formed directly in the halogenation process.

The halogenated acids have a higher refractive index than the original fatty acids, and hence, are desirable as delustering agents or intermediates in the preparation thereof. Their solubilities are also appreciably greater than those of the original fatty acids. The halogenated products, preferably chlorinated, are suitable as plasticizers or for lubricating purposes, either alone or in addition to mineral or vegetable oils. The acids or their derivatives, such as their esters, may be so employed in preparing metal

working or cutting lubricants, as well as lubricants for engines. The products possess germicidal properties and can be used in various bactericidal and/or insecticidal compositions. They are highly resistant to rancidity and serve as valuable addition agents to other fatty acids, soaps, or other derivatives thereof which tend to become rancid, to prevent these materials from so deteriorating.

Although the specific examples given hereinbefore describe the separation of the halogenated derivatives from the non-halogenated derivatives by fractional crystallization, other suitable methods such as the distillation of the fatty acids or the esters may be employed. Since the physical properties of these compounds are materially altered by the introduction of halogen substituents into their structure, it is possible to apply any of the numerous physical methods of separation, either to the fatty acids or to their derivatives, such as the esters (e. g., methyl, ethyl or glyceryl) and salts. These methods take advantage of the differences in boiling points, melting points, and relative solubilities of the various acids and derivatives so that the individual materials may be more readily separated into relatively pure fractions.

The process may be applied to any source of fatty acid or derivative thereof such as fats, fatty oils, oxidized mineral oil, by-products of paper manufacture, ester-waxes, and the like. Among the materials which may be treated by the present process are tallow, palm oil, olive oil, coconut oil, certain grades of Chinese vegetable tallow, cottonseed oil, whale oil, fish oils, and garbage grease; castor oil, montan wax, sperm oil, carnauba wax, opal wax, Japan wax, Chinese wax, tall oil, and the like, as well as the fatty acid mixtures derived from these compositions. The term "fatty acid compound" as used in this specification and the appended claims is to be understood to include the fatty acids as well as the suitable derivatives thereof. It is often desirable in the treatment of these fatty acid compounds, especially those containing other constituents than fatty acid derivatives, such as tall oil, to fractionate the product to concentrate the desired fraction of individual fatty acids. This may be accomplished by straight fractional distillation to remove undesired heads and/or tails which may adversely affect the halogenation reactions, or it may include a fractionation treatment to remove unsaponifiables such as those methods described in detail in the U. S. Patents 1,918,603 and 1,951,511 to Ittner. These fractionation processes may also be used in combination in either order to remove unsaponifiable constituents and other acids of appreciably different properties.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not intend to limit ourselves to the specific embodiments thereof except as indicated in the appended claims.

We claim:

1. The method of preparing relatively pure stearic acid and monochlorinated palmitic acid from a mixture containing stearic acid and palmitic acid which comprises treating such a mixture with a chlorinating agent in a quantity just sufficient to monochlorinate substantially all of the palmitic acid in the mixture, and then separating the monochloropalmitic acid from the stearic acid.

2. The process of separating individual fatty acid compounds from mixtures thereof which comprises treating a composition containing a mixture of fatty acid compounds with a halogenating agent in a quantity sufficient and under conditions whereby substantially all of the most halogen-reactive compound is substantially solely halogenated, and utilizing the properties of the halogenated compound to separate it from the remaining non-halogenated compounds.

3. The process of separating individual fatty acid compounds from mixtures thereof which comprises treating a composition containing a mixture of fatty acid compounds with a chlorinating agent until substantially all of the most reactive individual fatty acid compound in the mixture is substantially solely chlorinated, and then separating said chlorinated compound from said mixture.

4. The process of separating individual fatty acids from mixtures thereof which comprises treating a composition containing a mixture of fatty acids with a halogenating agent until substantially all of the most reactive individual fatty acid in the mixture is substantially solely halogenated, and then separating said halogenated fatty acid from said mixture.

5. The process of separting individual fatty acids from mixtures thereof which comprises treating a composition containing a mixture of fatty acids with a chlorinating agent until substantially all of the most reactive individual fatty acid in the mixture is substantially solely chlorinated, and then separating said chlorinated fatty acid from said mixture.

6. The process of separating individual fatty acid esters from mixtures thereof which comprises treating a composition containing a mixture of fatty acid esters with a halogenating agent until substantially all of the most reactive individual fatty acid ester in the mixture is substantially solely halogenated, and then separating said halogenated fatty acid ester from said mixture.

7. The process of separating individual fatty acid compounds from mixtures thereof which comprises fractionating a composition containing a mixture of fatty acid compounds to concentrate the individual compounds desired, treating a fraction containing a mixture of the desired fatty acid compounds with a halogenating agent until substantially all of the most reactive individual fatty acid compound in the mixture is substantially solely halogenated, and then separating said halogenated compound from said mixture.

8. The process of separating individual fatty acids from mixtures containing fatty acids which comprises fractionating a composition containing a mixture of fatty acids to concentrate the individual compounds desired, treating a fraction containing a mixture of the desired fatty acids with a halogenating agent until substantially all of the most reactive individual fatty acid in the mixture is substantially solely halogenated, and then separating said halogenated compound from said mixture.

9. The process of separating individual fatty acids from mixtures containing fatty acids which comprises fractionating a composition containing a mixture of fatty acids to concentrate the individual compounds desired, treating a fraction containing a mixture of the desired fatty acids

with a chlorinating agent until substantially all of the most reactive individual fatty acid in the mixture is substantially solely chlorinated, and then separating said chlorinated fatty acid from said mixture.

10. The process of separating individual fatty acid compounds from mixtures thereof which comprises treating a composition containing a mixture of fatty acid compounds with a halogenating agent until substantially all of the most reactive individual fatty acid compound in the mixture is substantially solely halogenated, separating said halogenated compound from said mixture, again treating the remaining mixture with a halogenating agent until substantially all of the next most reactive individual fatty acid compound in the mixture is substantially solely halogenated, separating said halogenated compound from the mixture, repeating this procedure until the mixture has been separated into the individual fatty acid compounds.

11. The process of separating individual fatty acids from mixtures thereof which comprises treating a composition containing a mixture of fatty acids with a chlorinating agent until substantially all of the most reactive individual fatty acids in the mixture is substantially solely chlorinated, separating said chlorinated fatty acid from said mixture, again treating the remaining mixture with a chlorinating agent until substantially all of the next most reactive individual fatty acid in the mixture is substantially solely chlorinated, separating said chlorinated fatty acid from the mixture, repeating this procedure until the mixture has been separated into the individual fatty acid constituents.

12. The process of separating individual fatty acid esters from mixtures thereof which comprises treating a composition containing a mixture of fatty acid esters with a halogenating agent until substantially all of the most reactive individual fatty acid ester in the mixture is substantially solely halogenated, separating said halogenated fatty acid ester from said mixture, again treating the remaining mixture with a halogenating agent until substantially all of the next most reactive individual fatty acid ester in the mixture is substantially solely halogenated, separating said halogenated fatty acid ester from the mixture, repeating this procedure until the mixture has been separated into the individual fatty acid ester constituents.

JOHN ROSS.
HANS GEORGE KIRSCHENBAUER.