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NITRIC ACID OXIDATION OF FATTY MATERIALS

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This invention relates to the oxidative scission of unsaturated and hydroxylated fatty compounds, and particularly to the oxidation of such compounds to form lower mono and dibasic acids.

It has heretofore been proposed to subject unsaturated fatty acids to the action of nitric acid, whereby to cut the fatty chains at the unsaturated linkages and to form mono and dibasic acids from the segments of the cut fatty chains. To accelerate this reaction, there have been proposed various catalysts such as compounds of mercury, copper, iron, and latterly, vanadium. However, it is impossible, even with the use of these catalysts, to obtain high yields of the mono and dibasic acids or to obtain even moderate yields in a reaction of reasonably short duration.

Accordingly, it is an object of this invention to provide a process for oxidative scission of fatty materials which will give high yields of desirable products.

Another object is to provide a process for oxidative scission of fatty materials which will not require an excessive length of time.

Still another object is to provide a process by which hydroxylated fatty materials, as well as unsaturated fatty materials, may be subjected to oxidative scission to yield mono and dibasic acids.

The above and other objects are attained by this invention in a process which involves treating a hydroxylated and/or unsaturated fatty starting material with nitric acid in the presence of a catalyst comprising a manganese compound. The fatty chains of the fatty materials are thereby cut at the unsaturated or hydroxyl-carrying carbons, and the carbons at the cut ends oxidized to carboxyl groups with the formation of mono and dicarboxylic acids. The fatty acids are separated from each other and from the unreacted materials and by-products by any suitable means, such as extraction, steam distillation or the like.

Referring to the hydroxylated and/or unsaturated fatty starting material, this may be any oil, fat, fatty acid or fatty ester containing fatty chains having carbinol or unsaturated groups intermediate the ends of such chains. In general, it is preferred to employ the unsaturated and/or hydroxylated fatty acids as starting materials in the practice of this invention, as such materials yield dibasic acids directly upon oxidative scission. Likewise, hydroxylated fatty materials are preferred to the unsaturated fatty materials, as the reaction proceeds more rapidly and smoothly and gives better yields than in the case of the unsaturated fatty materials. Examples of suitable hydroxylated acids are 12-hydroxy stearic

acid; 10-hydroxy stearic acid; ricinoleic acid, 9,10-dihydroxy stearic acid; 9 or 10-hydroxy palmitic acid; 9-hydroxy stearic acid, 13 or 14-hydroxy behenic acid and the like. Examples of suitable unsaturated acids are oleic acid, brassidic acid, erucic acid, linoleic acid, eleostearic acid, linolenic acid, clupanodonic acid and the like.

Instead of the pure acids there may be employed the mixed acids derived by hydrolysis of unsaturated and/or hydroxylated fats and oils, such as, for instance, the fatty acids derived by hydrolysis of castor oil, olive oil, hydrogenated castor oil, sardine oil and the like. Suitable fatty acids may likewise be produced by the hydrolysis of fatty materials which have been processed to develop hydroxyl or unsaturated groups therein, for instance wet-blown oils and fats or oils and fats which have been sulfonated and subjected to hydrolytic desulfonation. Examples of oils which when wet-blown may serve as sources of fatty acids suitable as starting materials in the process of this invention are cottonseed oil, corn oil, coconut oil, lard oil, peanut oil and the like. Examples of oils which when sulfonated and hydrolytically desulfonated may serve as sources of fatty acids suitable as starting materials in the process of this invention are olive oil, soyabean oil, castor oil, teaseed oil, sardine oil, train oil and the like.

Obviously, instead of pure esters there may be employed as starting materials in the process of this invention mixtures of suitable esters such, for example, as the natural and processed fats and oils named above as sources of fatty acids.

Referring to the manganese catalyst compound, this may most advantageously be supplied as manganese dioxide. However, instead of manganese dioxide, any manganous or manganic salt, or any manganese oxide, or any salt of any manganese-containing acid radical, may be employed. Examples of suitable manganese compounds coming within the above requirements are manganous chloride, manganic nitrate, manganous oxide, manganic oxide, manganese trioxide, manganese heptoxide, potassium permanganate, sodium manganite and the like.

The oxidation reaction is preferably carried out by mixing the manganese catalyst compound with the fatty material to be oxidized, heating the mixture to between about 60° and 120° C., preferably between 90° and 110° C. and thereafter slowly adding nitric acid with stirring. The nitric acid should be added with extreme slowness at first, until the induction period is over. The temperature is maintained between 60° and

120° C. and preferably between about 90° and about 110° C. for from about two hours to about six hours, after which the reaction mass is cooled and diluted with water to arrest the reaction. Based on the weight of the fatty starting material, there should be employed upwards of 3%, and preferably between about 0.5% and 25%, of catalyst. The amount of HNO₃ employed should be upwards of about five times the amount theoretically required to cut the fatty chains and oxidize the carbon atoms at the cut ends to carboxyl groups. The strength of the nitric acid employed will vary upwards of about 60% and should preferably be between about 65% and about 71%.

The monobasic acids may be recovered from the reaction mixture by steam distillation. In this case the reaction mixture, after dilution to arrest the reaction, is neutralized with a suitable base, slightly acidified, then subjected to steam distillation, the monobasic acids coming over with the steam, leaving behind the dibasic acids, by-products and unreacted material.

The dibasic acids are preferably recovered from the steam distillation residue by a process depending upon the solubility of the dibasic acids in slightly acid solution. It has been discovered that the dibasic acids dissolve in solutions which have a sufficiently high acidity to suppress solution of the monobasic acids and other materials in the residue. A pH between about 5.5 and about 6.5 will usually effect solution of the dibasic acids, while suppressing solution of the other constituents, but obviously this will vary with the materials treated and can best be determined in each individual case by experiment. The separation process based upon the principles above set forth may be carried out by adjusting the pH of the steam distillation residue to a value (usually between about 5.5 and about 6.5) such as to cause the dibasic acids to dissolve in the aqueous phase; thereafter removing the aqueous solution of the dibasic acids from the undissolved residue; and finally reacidifying the aqueous solution to cause the dibasic acids to be thrown out of solution. The dibasic acids are then removed and dried.

The dibasic acids may also be recovered from the steam distillation residue by any other suitable process such as a selective solvent extraction process. For instance, the residue may be extracted first with a non-polar, or relatively slightly polar, solvent such as a petroleum fraction to remove the unreacted oil and by-products without dissolving the dibasic acids. Thereafter the residue may be extracted with a relatively more highly polar solvent, such as ethyl acetate, to dissolve the dibasic acids. Upon evaporation of the polar solvent extraction solution, the dibasic acids are left as a technically pure product. This product may be further refined and purified by recrystallization or other means.

A petroleum fraction was cited above as a suitable non-polar solvent; however, ethylene dichloride, chloroform, cold benzene, cold ether and other solvents of like character may be employed. Ethyl acetate was cited as a suitable relatively highly polar solvent; however, butanol, hot water, hot methanol, hot ethanol, hot ether or the like may be substituted therefor.

The process as above outlined commonly produces yields in excess of 60% of the theoretical, and in the treatment of hydroxylated fatty materials produces yields in excess of 70% or 80% of the theoretical. Further, the process may be

carried out much more expeditiously than any of the heretofore known processes for oxidative scission of fatty materials. With the above discussion in mind, there are given hereinafter examples of procedures according to this invention, which examples are to be taken as illustrative merely, and not in any limiting sense. All parts given are by weight.

Example I

30 parts of the fatty acids derived by hydrolysis of hydrogenated castor oil were melted and .3 part of MnO₂ were mixed in at 113° C. 95 parts of 70% HNO₃ were then added slowly, with continuous stirring, the first portions being added dropwise until the reaction was going smoothly. The mixture was maintained at 105° C. for 4½ hours. The mixture was then cooled, diluted with 300 parts of water, neutralized with NaOH and then slightly acidified. The acidified mixture was steam distilled and 7 parts of monobasic acids, largely caproic acid, were recovered. The residue from the steam distillation was extracted with 150 parts of petroleum ether (boiling range 35° to 70° C.) to remove the unreacted fatty materials and by-products. The extracted residue was then re-extracted with ethyl acetate, and the extract solution evaporated to leave 19 parts of a white solid consisting principally of mixed decane dicarboxylic and nonanedicarboxylic acids. The mixed dicarboxylic acids melted between 95° C. and 108° C.

Example II

60 parts of 10-hydroxy stearic acid (produced by the sulfonation and hydrolysis of oleic acid) were melted and heated to 90° C., and .3 part of MnO₂ were added. 95 parts of 70% HNO₃ were then added slowly with continuous stirring, the first portions being added dropwise until the reaction was proceeding smoothly. The mixture was maintained at 90° C. for 3½ hours. The resultant oxidized mass was then cooled, diluted, neutralized, reacidified, steam distilled, and extracted with petroleum ether and ethyl acetate exactly as in Example I. There were recovered 12 parts of monobasic acids and 15 parts of mixed dibasic acids melting between 78° C. and 99° C.

Example III

60 parts of the fatty acids derived by hydrolysis of castor oil and 1 part MnO₂ were mixed and heated to 100° C. 190 parts of 70% HNO₃ were added slowly, using the same precautions as were exercised in the preceding examples. The mass was maintained between 90° C. and 100° C. for 5½ hours. The resultant oxidized mass was then cooled, diluted with 300 parts of water, and sufficient 10% NaOH added to leave the mass only slightly acid. The mass was then subjected to steam distillation, and 13 parts of monobasic acids were recovered in the distillate. The pH of the residue from the distillation was adjusted with NaOH to 6.5, whereupon the monosodium salts of the dibasic acids passed into solution and the unreacted fat and by-products were thrown out of solution. The solution was removed from the insoluble matter and acidified. 18 parts of dibasic acids (mostly azelaic and suberic acids) separated from the solution. These mixed acids melted between 95° C. and 105° C.

Example IV

31 parts of 9,10-dihydroxy stearic acid were melted and heated to 100° C. and .5 part of

MnO₂ were added. 47 parts of 70% HNO₃ were stirred in width the same precautions as in the preceding examples, and the mixture heated to 110° C. for 5 hours. The resultant mass was cooled, diluted, partially neutralized, steam distilled and adjusted to a pH of 6.5, and the solution removed and acidified exactly as in Example III. There were recovered 6 parts of monobasic acids and 10 parts of mixed dibasic acids (mostly azelaic and suberic acids). The mixed dibasic acids melted between 106° and 125° C.

Example V

56 parts of oleic acid and .6 parts of MnO₂ were mixed and heated to 80° C. 190 parts of 70% HNO₃ were added with the same precautions as in the other examples. The temperature was maintained at 80° C. for 4 hours. The resultant mass was cooled, diluted, partially neutralized, steam distilled, and adjusted to a pH of 6.5, and the solution removed and reacidified exactly as in Example III. There were recovered 5 parts of monobasic acids and 14 parts of mixed dibasic acids (mostly azelaic and suberic acids), these mixed acids melting between 65° C. and 77° C. After recrystallization from benzene, the mixed dibasic acids melted between 88° C. and 102° C.

It will thus be seen that there is provided by this invention a process for oxidizing fatty materials, and especially hydroxylated fatty materials, to produce short chain mono and dibasic acids in much higher yields than are obtained by older processes. Further, the processes of this invention can be carried out very much more expeditiously than any older processes.

Since certain changes in carrying out the above process may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having described our invention what we claim as new and desire to secure by Letters Patent is:

1. Process for oxidizing fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

2. Process for oxidizing fatty substances containing hydroxylated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

3. Process for oxidizing fatty substances containing the fatty residues of hydroxystearic acid, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

4. Process for oxidizing fatty substances containing the fatty residues of dihydroxystearic acid, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

5. Process for oxidizing fatty substances containing unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from

the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

6. Process for oxidizing fatty substances containing the fatty residues of oleic acid, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

7. Process for oxidizing fatty acids containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said acids with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

8. Process for oxidizing fatty acids containing hydroxylated fatty residues, which comprises treating said acids with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

9. Process which comprises treating hydroxystearic acid with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

10. Process which comprises treating dihydroxystearic acid with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

11. Process for oxidizing fatty acids containing unsaturated fatty residues, which comprises treating said acids with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

12. Process which comprises treating oleic acid with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles.

13. Process for oxidizing fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of manganese dioxide.

14. Process for oxidizing fatty substances containing hydroxylated fatty residues, which comprises treating said substances with nitric acid in the presence of manganese dioxide.

15. Process for producing mono and dibasic acids from fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles; and separating from the resultant oxidized mass the monobasic and dibasic acids formed by the oxidation of the fatty substances.

16. Process for producing mono and dibasic acids from fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises

treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles; separating the monobasic acids from the resultant oxidized mass and extracting the residue of the oxidized mass with a non-polar organic solvent to remove the unreacted fatty materials and by-products; and further extracting said residue with a polar organic solvent to recover the dibasic acids therefrom.

17. Process for producing mono and dibasic acids from fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles; separating the monobasic acids from the resultant oxidized mass; adjusting the pH of the residual mass to a value sufficiently high to effect solution of the dibasic acids in the aqueous phase of the mass, but sufficiently low to suppress solution of the other materials; and separating from the mass the aqueous phase containing the dibasic acids.

18. Process for producing mono and dibasic acids from fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-con-

taining acid radicles; and subjecting the resultant oxidized mass to steam distillation to separate the monobasic acids therefrom.

19. Process for producing mono and dibasic acids from fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a compound selected from the group consisting of manganous salts, manganic salts, manganese oxides and salts of manganese-containing acid radicles; subjecting the resultant oxidized mass to steam distillation to separate the monobasic acids therefrom; extracting the distillation residue with a non-polar organic solvent to remove the unreacted fatty materials and by-products; and further extracting the distillation residue with a polar organic solvent to recover the dibasic acids therefrom.

20. Process for producing mono and dibasic acids from fatty substances containing residues chosen from the group consisting of hydroxylated and unsaturated fatty residues, which comprises treating said substances with nitric acid in the presence of a manganese compound; subjecting the resultant oxidized mass to steam distillation to separate the monobasic acids therefrom; adjusting the pH of the residual mass to a value sufficiently high to effect solution of the dibasic acids in the aqueous phase of the mass, but sufficiently low to suppress solution of the other materials; and separating from the mass the aqueous phase containing the dibasic acids.

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