



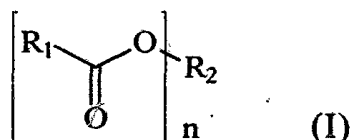
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PROCESS FOR THE PREPARATION OF MONO- AND DICARBOXYLIC ACIDS FROM UNSATURATED FATTY ACIDS AND/OR THEIR DERIVATIVES
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1. A process for preparation of mono- and dicarboxylic acids from unsaturated fatty acids and/or their derivatives, comprising the following stages:

- a stage which consists in oxidizing an unsaturated fatty acid in the form of acid and/or of ester containing at least one double bond corresponding to the formula (I):



in which:

- n is a number equal to 1, 2 or 3,
- R₁ denotes a linear or branched alkenyl or alkadienyl radical containing from 4 to 40 carbon atoms,
- R₂ may take the following meanings:
 - if n = 1, R₂ denotes a hydrogen atom or an alkyl radical, optionally carrying one or more hydroxyl groups,

if $n = 2$, R_2 denotes an alkylene or alkenylene radical, optionally carrying one or more hydroxyl groups,

if $n = 3$, R_2 denotes an alkyl radical containing 3 carbon atoms, using hydrogen peroxide, in the presence of a metal oxide or of a carboxylic acid optionally used in combination with a ruthenium-based catalyst,

- a stage which consists in reacting the reaction mixture originating from the preceding stage with nitric acid in the presence of a vanadium-based catalyst, optionally used in combination with a cocatalyst, and then

- a stage of recovery of the mono- and dicarboxylic acids.

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C O M P L E T E S P E C I F I C A T I O N

FOR A STANDARD PATENT

O R I G I N A L

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Invention Title: "PROCESS FOR THE PREPARATION OF MONO- AND
DICARBOXYLIC ACIDS FROM UNSATURATED FATTY
ACIDS AND/OR THEIR DERIVATIVES"

The following statement is a full description of this invention,
including the best method of performing it known to us:-

PROCESS FOR THE PREPARATION OF MONO- AND DICARBOXYLIC
ACIDS FROM UNSATURATED FATTY ACIDS AND/OR THEIR
DERIVATIVES

The present invention relates to a process
5 for the preparation of carboxylic acids from
unsaturated fatty acids and/or their derivatives.

More precisely, the invention relates to a
process for the preparation of monofunctional and
difunctional aliphatic carboxylic acids from
10 unsaturated fatty acids in the form of acid or of ester
and more particularly in the form of triglyceride.

Various processes have been proposed for
carrying out the preparation of carboxylic acids from
unsaturated fatty acids.

15 A relatively old process described in
US-A-2 773 095 consists in performing the oxidation of
the latter compounds by subjecting them to an oxidation
with the aid of dilute nitric acid under pressure. The
oxidation of oleic acid results in pelargonic acid and
20 azelaic acid being obtained. However, the selectivity
of the reaction conducted according to US-A-2 773 095
is poor because an overoxidation is observed, resulting
in the formation of lower monoacids and diacids.

Furthermore, it is known according to
25 US-2 865 937 to prepare mono- and dicarboxylic acids
from unsaturated fatty acids, especially oleic acid, by
subjecting the starting substrate to a scission by

ozonolysis, followed by an oxidising decomposition. A major disadvantage of this type of process is its prohibitive cost resulting from the use of ozone.

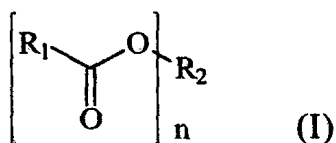
Another, equally costly, process is described in FR-A 2 101 729. An example of preparation mentions the oxidation of oleic acid with hydrogen peroxide, followed by
5 hydrolysis with sulphuric acid, separation using solvent and another oxidation stage performed using a percarboxylic acid in the presence of metal ions. Besides the number of stages described, the high cost of the reactants engaged has to be noted.

All these processes are not satisfactory because they are difficult to transpose to an industrial scale, either because of poor reaction yields or for economic reasons.

10 The objective of the present invention is to provide a process enabling the abovementioned disadvantages to be avoided.

According to a first aspect of the invention, there is provided a process for preparation of mono- and dicarboxylic acids from unsaturated fatty acids and/or their derivatives, comprising the following stages:

15 - a stage which consists in oxidizing an unsaturated fatty acid in the form of acid and/or of ester containing at least one double bond corresponding to the formula (I):



in which:

- n is a number equal to 1, 2 or 3,
- 20 - R₁ denotes a linear or branched alkenyl or alkadienyl radical containing from 4 to 40 carbon atoms,
- R₂ may take the following meanings:



if $n = 1$, R_2 denotes a hydrogen atom or an alkyl radical, optionally carrying one or more hydroxyl groups,

if $n = 2$, R_2 denotes an alkylene or alkenylene radical, optionally carrying one or more hydroxyl groups,

5 if $n = 3$, R_2 denotes an alkyl radical containing 3 carbon atoms using hydrogen peroxide, in the presence of a metal oxide or of a carboxylic acid optionally used in combination with a ruthenium-based catalyst,

- a stage which consists in reacting the reaction mixture originating from the preceding stage with nitric acid in the presence of a vanadium-based catalyst, optionally
- 10 used in combination with a cocatalyst, and then
- a stage of recovery of the mono- and dicarboxylic acids.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense

15 of "including, but not limited to".

A process for the preparation of mono- and dicarboxylic acids from unsaturated fatty acids and/or their derivatives has now been found, and it is this that forms the subject of the present invention, the process being characterized in that it comprises the following stages:

- 20 - a stage which consists in oxidizing an unsaturated fatty acid in the form of acid and/or of ester using hydrogen peroxide, in the presence of a metal oxide or of a



carboxylic acid optionally used in combination with a ruthenium-based catalyst,
- a stage which consists in reacting the reaction mixture originating from the preceding stage with nitric acid in the presence of a vanadium-based catalyst, optionally used in combination with a cocatalyst, and then
- a stage of recovery of the mono- and dicarboxylic acids.

The process of the invention comprises a first operation of controlled oxidation of the starting substrate, thus making it possible to limit the consumption of hydrogen peroxide leading to an intermediate product in which the double bonds are oxidized to an epoxy bridge and/or to two vicinal hydroxyl groups.

Without isolation of the intermediate product, a stage of scission and of oxidizing hydrolysis performed using nitric acid is linked into a sequence, thus making it possible to obtain the desired mono- and dicarboxylic acids.

The process of the invention is particularly advantageous because it makes it possible to obtain the said acids with a good reaction selectivity.

In addition, it entails a reactant cost which is wholly compatible with industrial use.

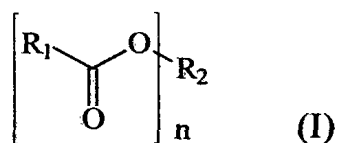
Finally, another advantage, which is by no

means a minor one, is that it can be applied not only with unsaturated fatty acids, for example oleic acid, but also by starting from unsaturated fatty acids in the form of triglycerides, and this makes it possible to start directly from oils or from fats that contain them.

5 The process of the invention thus makes it possible to make profitable use of oils, especially rapeseed and sunflower oils which may be available on the market in a large quantity.

The process of the invention applies to any fatty acid containing at least one double bond.

10 It may be symbolized by the formula (I):



in which:

- n is a number equal to 1, 2 or 3,
- R₁ denotes a linear or branched alkenyl or alkadienyl radical containing from
15 4 to 40 carbon atoms,
- R₂ may take the following meanings:
 - if n = 1, R₂ denotes a hydrogen atom or an alkyl radical, preferably containing from 1 to 6 carbon atoms, optionally carrying one or more hydroxyl groups,
 - if n = 2, R₂ denotes an alkylene or _____



alkenylene radical, preferably containing from 1 to 6 carbon atoms, optionally carrying one or more hydroxyl groups, if $n = 3$, R_2 denotes an alkyl radical containing 3 carbon atoms.

The compounds used preferably correspond to the formula (I) in which R_1 denotes an alkenyl radical containing from 6 to 22 carbon atoms and containing from 1 to 5 double bonds, preferably 1 to 3, and R_2 denotes a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms optionally carrying from 1 to 2 hydroxyl groups where $n = 1$, a diethylene or propylene radical optionally carrying a hydroxyl group where $n = 2$, or a 1,2,3-propanetriyl radical where $n = 3$.

Examples of unsaturated fatty acids which may be mentioned are the unsaturated fatty acids containing only one double bond, such as linderic acid, myristoleic acid, palmitoleic acid, oleic acid, petroselenic acid, doeglic acid, gadoleic acid and erucic acid, unsaturated fatty acids containing two double bonds, such as linoleic acid, unsaturated fatty acids containing three double bonds, such as linolenic acid, unsaturated fatty acids containing more than four double bonds, such as isanic acid, stearodonic acid, arachidonic acid and chypanodonic acid, and unsaturated fatty acids carrying a hydroxyl group, such as ricinoleic acid, and mixtures thereof.

Among the abovementioned acids the following fatty acids are preferably used: palmitoleic acid, oleic acid, petroselenic acid, erucic acid, linoleic acid, linolenic acid and ricinoleic acid.

5 A natural source of the fatty acids are oils and fats.

In fact, the process of the invention is particularly advantageous because it makes it possible to start from natural oils and fats, which are glycerol esters. They contain mixtures of fatty acid triglycerides generally mixed with saturated fatty acids.

10

Sources of animal origin which may be mentioned are, among others, sperm whale oil, dolphin oil, whale oil, seal oil, sardine oil, herring oil, dogfish oil, cod liver oil, neat's-foot oil and beef, pork, horse and mutton fats (tallows).

15

Examples of sources of vegetable oils which may be mentioned are, among others, rapeseed oil, sunflower oil, groundnut oil, olive oil, nut oil, corn oil, soya oil, linseed oil, hemp oil, grapeseed oil, copra oil, palm oil, cottonseed oil, babassu oil, jojoba oil, sesame oil and castor oil.

20

The oils mentioned below are used preferentially in the process of the invention: rapeseed oil, sunflower oil, soya oil, linseed oil and castor oil.

25

It is also possible to start from the esters

corresponding to the said acids, in particular the methyl, ethyl and propyl esters, and more particular mention may be made of the products of methanolysis especially of the oils and more preferably of rapeseed oils.

In the following description of the present invention the term "unsaturated fatty acid" will be employed generically and will refer to both the unsaturated fatty acids strictly speaking, by themselves or mixed, and their ester or triglyceride form.

In accordance with the process of the invention the oxidation of the unsaturated substrate is performed with hydrogen peroxide.

The hydrogen peroxide used according to the invention may be in the form of an aqueous solution.

The concentration of the aqueous solution of hydrogen peroxide is generally at least 20 % by weight of H_2O_2 and, preferably, between 20 and 70 % by weight.

The quantity of hydrogen peroxide used is a function of the number of double bonds to be oxidized which are present in the starting substrate. A quantity equal to the stoichiometry or a slight excess ranging from 0 to 50 %, preferably between 1 and 20 %, is generally used.

The first stage of the process of the invention may be conducted according to various alternative forms which differ in what is used in

One embodiment of the invention consists in adding a carboxylic acid to the hydrogen peroxide, thus permitting the in-situ formation of a peracid.

5 The carboxylic acids liable to be used may be mono- or polycarboxylic. They are compounds which do not contain unsaturations.

They correspond more particularly to the following general formula (II):

10 R_3 -COOH (II),

in the said formula (II), R_3 denotes a hydrocarbon radical containing from 1 to 22 carbon atoms, which may be a linear or branched, saturated acyclic aliphatic radical or a monocyclic or polycyclic saturated cycloaliphatic radical.

The said radical R₃ may carry another COOH functional group. It may also carry other substituents, for example alkoxy or halogen, provided that they do not interfere in the reaction.

20 R_3 denotes more particularly a linear or branched alkyl radical containing from 1 to 22 carbon atoms or a cycloalkyl radical containing from 5 to 7 carbon atoms.

Examples which may be mentioned of carboxylic acids liable to be used in the process of the invention are aliphatic monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid and hexanoic acid, aliphatic dicarboxylic acids such as

succinic acid and adipic acid, and cycloaliphatic acids such as cyclopentanecarboxylic acid and cyclohexanecarboxylic acid.

Among the abovementioned carboxylic acids those preferably used are saturated aliphatic carboxylic acids, preferably formic acid or acetic acid.

It is also advantageous to use a carboxylic acid which is recovered in the products formed in the course of the process of the invention and pelargonic acid, azelaic acid and stearic acid may be mentioned more particularly.

It will not constitute a departure from the scope of the present invention to use either a percarboxylic acid directly instead of preparing it in situ, or a precursor of a carboxylic acid which would produce the latter in the oxidizing reaction conditions.

The quantity of carboxylic acid used may vary within wide limits. It may range from a catalytic quantity to a stoichiometric quantity.

More precisely, the molar ratio of hydrogen peroxide to the carboxylic acid varies between 10 and 500 %, preferably between 10 and 40 %.

According to a modified alternative form, it is also possible according to the invention to perform the oxidation of the unsaturated fatty acid, using hydrogen peroxide, in the presence of carboxylic acid

and of a ruthenium-based catalyst.

Any ruthenium compound may be used as catalyst.

Examples which may be mentioned of compounds
5 liable to be used as catalysts of the invention are,
among others, ruthenium(III) chloride, ruthenium(IV)
chloride, ruthenium pentafluoride, ruthenium(II) oxide,
ruthenium(IV) oxide, ammoniated ruthenium oxychloride
 $\text{Ru}_2(\text{OH})_2\text{Cl}_4 \cdot 7\text{NH}_3 \cdot 5\text{H}_2\text{O}$ and ruthenium acetate.

10 Ruthenium(III) chloride is preferably chosen
as ruthenium-based catalyst.

The quantity of ruthenium-based catalyst
which is used, expressed as the weight ratio of
hydrogen peroxide to the catalyst, may be
15 advantageously between 1 and 35 %, preferably between 3
and 10 %.

Another alternative form of embodiment of the
first stage of controlled oxidation involved in the
process of the invention consists in performing the
20 oxidation of the unsaturated fatty acid with hydrogen
peroxide in the presence of a catalyst based on a metal
of group VIa of the Periodic Classification of the
elements.

For the definition of the elements, reference
25 is made below to the Periodic Classification of the
elements published in the Bulletin de la Société
Chimique de France, No. 1 (1966).

A tungsten- and/or molybdenum-based catalyst

is preferably used.

The catalyst is preferably chosen from tungstic acid, phosphotungstic acid, molybdic acid and phosphomolybdic acid.

- 5 It is therefore preferably in acidic form. It is possible to start directly from the abovementioned compounds or else to form them in situ from their oxides or salts.

10 Examples of molybdenum-based catalysts which may be mentioned are especially:

- molybdenum halides, for example molybdenum hexafluoride, molybdenum tri-, tetra- or pentachloride and molybdenum di-, tri- or tetrabromide,
- molybdenum hydroxides $\text{Mo}(\text{OH})_3$, $\text{MoO}(\text{OH})_3$ or $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$,
- 15 - molybdenum oxides such as molybdenum dioxide, trioxide, pentaoxide or sesquioxide,
- molybdenum oxyhalides such as molybdenum oxydifluoride or oxytetrafluoride, molybdenum oxydichloride, oxytrichloride, oxytetrachloride,
- 20 oxypentachloride, molybdenum acid oxychloride and molybdenum oxydibromide,
- molybdenum metaphosphate,
- ammonium phosphomolybdate,
- ammonium molybdate.

25 Where the tungsten-containing catalyst is concerned, it is possible to start more particularly from:

- tungsten halides, for example tungsten hexafluoride,

tungsten di-, tetra-, penta- or hexachloride and

tungsten di-, penta- or hexabromide,

- tungsten oxides such as tungsten dioxide, trioxide, pentaoxide or sesquioxide,

5 - tungsten oxyhalides such as tungsten oxytetrafluoride, tungsten oxydichloride and oxytetrachloride and tungsten oxydibromide and oxytetrabromide,

- tungsten metaphosphate,

10 - ammonium tungstate,

- ammonium phosphotungstate.

The quantity of tungsten- and/or molybdenum-based catalyst used, expressed as the weight ratio of hydrogen peroxide to the catalyst, may be

15 advantageously between 1 and 35 %, preferably between 3 and 10 %.

The formation of the catalysts in acid form takes place when starting from the abovementioned compounds, by addition of a small quantity of strong
20 acid.

A strong acid refers, in the present invention, to an acid which has a pKa in water lower than -0.1 and preferably lower than -1.0.

The pKa is defined as the ionic dissociation
25 constant of the acid/base pair when water is employed as solvent.

There may be mentioned more particularly the oxyacids, whether containing halogen or not, such as

nitric acid, sulphuric acid, pyrosulphuric acid,
phosphoric acid, polyphosphoric acids, perchloric acid,
halosulphonic acids such as fluorosulphonic acid,
chlorosulphonic acid or trifluoromethanesulphonic acid,
5 methanesulphonic acid, ethanesulphonic acid,
ethanedisulphonic acid, benzenesulphonic acid,
benzenedisulphonic acids, toluenesulphonic acids,
naphthalenesulphonic acids and naphthalenedisulphonic
acids.

10 Nitric acid, sulphuric acid or phosphoric
acid is chosen very particularly among these acids.

The quantity of strong acid which is used,
expressed as the weight ratio of the strong acid to
hydrogen peroxide, may be advantageously between 1 and
15 50 %, preferably between 5 and 20 %.

The first oxidation stage is performed at a
temperature which is advantageously between 30 and
100°C, preferably between 60°C and 100°C.

The process of the invention is generally
20 carried out at atmospheric pressure, but it may also be
carried out at pressures which are higher or lower than
atmospheric pressure.

From a practical viewpoint, the process of
the invention is easy to carry out. The various
25 reactants are charged. There is no order of
introduction to be followed, only it is preferred to
add the hydrogen peroxide, using gradual, continuous or
portionwise addition to a reaction mixture containing

the substrate, the carboxylic acid and the catalysts if necessary.

At the end of reaction an intermediate product is obtained in which the double bonds are
5 oxidized to an epoxy bridge and/or to two vicinal hydroxyl groups.

According to the process of the invention the intermediate product is not isolated and the next stage of scission and of oxidizing hydrolysis performed using
10 nitric acid is directly linked into a sequence.

An aqueous solution of nitric acid which may be of any concentration and which may vary between 30 % and 100 % is used. However, a concentration of between 40 % and 60 % is preferred.

15 The nitric acid is used in a large excess. The quantity of nitric acid represents from 2 to 50 times the weight of the starting substrate and, more preferably, from 4 to 10 times.

It is preferable to include a generator of
20 NO^+ in order to initiate the nitric oxidation. Accordingly, it is possible to start from nitrogen dioxide NO_2 , from nitrogen trioxide N_2O_3 , from nitrogen peroxide N_2O_4 or from nitrogen oxide NO . In the case where the said agent is gaseous in the reaction
25 conditions, it is bubbled into the mixture.

It is also possible to make use of nitrous acid, of a nitrosylsulphate or nitrosylsulphuric acid or of a nitrous salt, preferably an alkali metal, and

still more preferentially a sodium, salt.

The quantity of this agent may vary widely. It is advantageously between 0 and 5 % of the weight of nitric acid, and preferably between 0 and 1 %.

5 As mentioned above, the nitric acid is employed in the presence of a vanadium-based catalyst.

One of the compounds listed below may be employed, as catalyst:

- vanadium halides such as vanadium tri-, tetra- or
10 pentafluoride, vanadium di-, tri- or tetrachloride or vanadium tribromide,
- vanadium oxides such as vanadium oxide, vanadium dioxide, vanadium sesquioxide or vanadium pentoxide,
- vanadium oxyhalides, in particular oxydi- or
15 trifluoride, vanadium oxymono-, di- or trichloride and vanadium oxymono-, di- or tribromide,
- vanadium sulphate,
- vanadyl sulphate,
- alkali metal or ammonium vanadates in the ortho, meta
20 or pyro form,
- vanadyl acetylacetonate.

This list does not constitute any limitation and it is also possible to make use of double salts containing vanadium.

25 Ammonium vanadates are preferably chosen as catalyst among the abovementioned compounds.

The quantity of vanadium-based catalyst used, expressed as the weight ratio of the catalyst,

expressed as HVO_3 , to nitric acid, is preferably between 0.001 and 1 %, preferably between 0.02 and 0.5 %.

As mentioned above, a metallic cocatalyst, the role of which is to accelerate the speed of reaction, may be added during this nitric oxidation stage conducted in the presence of a vanadium-based catalyst.

Use is made of a cocatalyst based on a metal of group VIIa and VIII of the Periodic Classification of the elements, and catalysts based on manganese, iron, nickel, ruthenium and cobalt may be mentioned by way of preference.

Examples of compounds liable to be used as cocatalysts which may be mentioned are, among others, the oxides, hydroxides, nitrates, halides, oxyhalides, phosphates, pyrophosphates, carbonates, carboxylates and alcoholates of the various abovementioned metals.

The preferred salts are the following:
iron(II) nitrate, iron(III) nitrate, nickel(II) nitrate, cobalt(II) nitrate, cobalt(III) nitrate, cobalt(II) acetate, manganese(II) carbonate and ruthenium(III) chloride.

The quantity of cocatalyst, expressed as the weight ratio of the cocatalyst to nitric acid, is preferably between 0.001 and 1 %, preferably between 0.02 and 0.5 %.

A preferred embodiment of the invention

consists in performing this nitric oxidation stage in the presence of oxygen or a gas containing it.

It is thus possible, throughout the reaction, to regenerate nitric acid from nitrous acid.

5 This gas may be pure oxygen or a gas containing it, preferably air. In the case of pure oxygen, this may be bubbled into the reaction mixture at a flow rate, for example, of 0.1 to 50 litres/hour.

10 The quantity of oxygen to be used is not critical, provided that it is such that neither the feed gas nor a possible gas phase liable to appear in the reaction zone is in the region of explosive compositions, bearing in mind the other chosen reaction parameters or conditions. The quantity of oxygen may be
15 in excess or in deficiency in relation to the stoichiometry of the reaction, in respect of the substrate to be oxidized.

 It is generally determined as a function of the number of double bonds to be oxidized. It is from
20 1 to 2 times the stoichiometric quantity when the starting substrate is an unsaturated fatty acid and from 5 to 8 times the stoichiometric quantity when the raw material is an oil or a fat.

 The pressure of oxygen or of the reaction air
25 varies between 1 and 10 bar.

 The process of the invention may be conducted at atmospheric pressure.

 In this second stage the reaction temperature

is chosen preferably between 40°C and 100°C and more preferably between 60 and 90°C.

As previously, the reaction is advantageously conducted at atmospheric pressure.

5 The invention is easy to carry out in practice.

According to a preferred method the catalyst and optionally the cocatalysts are placed in the nitric acid solution, which is then introduced into the
10 reaction mixture originating from the preceding stage.

The gas stream containing oxygen is then bubbled through.

At the end of reaction the reaction mixture is two-phase.

15 The aqueous phase contains the nitric acid, the various catalysts, cocatalysts and the carboxylic acids which are predominantly the saturated dicarboxylic acids.

The organic phase contains essentially the
20 saturated monocarboxylic fatty acids formed during the reaction and possibly those present initially, as well as the unsaturated fatty acids which have not reacted.

It should be noted that the process of the invention has the advantage of not degrading the
25 saturated fatty acids which may be present in the starting substrate, especially in the case of oils and fats.

The separation of the aqueous and organic

phases is undertaken preferably by settling while hot.

One or more washing operations of the organic phase are preferably performed with water in order to recover any saturated dicarboxylic fatty acids

5 remaining in the organic phase. The aqueous washings may be combined with the aqueous phase obtained in the separation of the organic and aqueous phases.

The aqueous phase containing the saturated dicarboxylic fatty acids is cooled by returning the
10 temperature to the ambient temperature.

The said carboxylic acids crystallize and are recovered by following conventional solid/liquid separation techniques, preferably by filtration.

The separation may be optionally followed by
15 one or more washing operation with water.

Furthermore, the organic phase is treated in order to remove the organic solvent by distillation.

The monocarboxylic acids are isolated from the organic phase by following conventional
20 liquid/liquid separation techniques, preferably distillation.

The aqueous phase which contains the nitric acid and the catalysts and cocatalysts may be advantageously recycled after evaporation of the excess
25 water, in order to obtain an adequate concentration of nitric acid.

The process of the invention is perfectly suitable for the preparation of pelargonic acid and

azelaic acid, which are obtained from oleic acid and rapeseed and sunflower oils.

Examples of practical implementation of the invention are given below.

- 5 The examples which follow illustrate the invention without, however, limiting it.

The yields mentioned in the examples correspond to the following definition:

- selectivity for azelaic acid: CY

10 number of moles of azelaic acid which are formed

$$CY = \frac{\text{number of moles of azelaic acid which are formed}}{\text{number of moles of azelaic + suberic + pimelic acid which are formed}}$$

- selectivity for pelargonic acid: CY

15 number of moles of pelargonic acid which are formed

$$CY = \frac{\text{number of moles of pelargonic acid which are formed}}{\text{number of moles of pelargonic + caprylic + heptanoic acids formed}}$$

Example 1:

- 20 In this example the oxidative scission of "oleic" sunflower oil is performed in the presence of formic acid and sulfuric acid.
- 828 mg of "oleic" sunflower oil are charged into a stirred reactor fitted with a condenser and a temperature probe.

- 25 The fatty acids composition of this sunflower oil is the following:

palmitic acid:	4.6 %
stearic acid:	4.8 %
oleic acid:	77.8 %
linoleic acid:	12.8 %

413 mg of an aqueous solution of 30% strength aqueous hydrogen peroxide, that is 3.64 mmol, 5 g of formic acid and 250 mg of 96% sulphuric acid are added.

The reaction mixture is kept at 45°C for 2 hours
5 and then at 80°C for 4 hours.

A reaction mixture based on nitric acid and made up of 13.2 ml of a 49% strength aqueous solution of nitric acid, 106 mg of ammonium metavanadate and 50 mg of sodium nitrite is then added slowly to this reaction
10 mixture. The reaction mixture is then kept at 75°C for 6 hours.

At the end of reaction the reaction mixture is cooled.

The pH is then brought to 2.4 by adding an aqueous
15 solution of sodium hydroxide at a concentration of 36 %.

The mixture is then made up to 500 ml and determined by capillary electrophoresis.

The results obtained are the following:

pelargonic acid:	236 mg
caprylic acid:	42 mg

heptanoic acid:	11 mg
azelaic acid:	117 mg
suberic acid:	13 mg
pimelic acid:	12 mg

The selectivity for azelaic acid is 82 %.

The selectivity for pelargonic acid is 82 %.

Example 2:

In this example the oxidative scission of "oleic"
 5 rapeseed oil is performed in the presence of formic acid and sulfuric acid.

830 mg of "oleic" rapeseed oil are charged into a stirred reactor fitted with a condenser and a temperature probe.

The fatty acids composition of this rapeseed oil
 10 is the following:

palmitic acid:	3.2 %
stearic acid:	2 %
oleic acid:	86.8 %
linoleic acid:	2.3 %
linolenic acid:	4.2 %
gadoleic acid:	1.5 %

410 mg of an aqueous solution of 30% strength aqueous hydrogen peroxide, that is 3.79 mmol, 5 g of formic acid and 250 mg of 96% sulphuric acid are added.

The reaction mixture is kept at 45°C for 2 hours

and then at 80°C for 4 hours.

A reaction mixture based on nitric acid and made up of 13.2 ml of a 49% strength aqueous solution of nitric acid, 106 mg of ammonium metavanadate and 50 mg of sodium nitrite is then added slowly to this reaction mixture. The reaction mixture is then kept at 75°C for 6 hours and then at 90°C for 2 hours.

At the end of reaction the reaction mixture is cooled.

10 The pH is then brought to 2.4 by adding a 36% strength aqueous solution of sodium hydroxide.

The mixture is then made up to 500 ml and analysed by capillary electrophoresis.

The results obtained are the following:

pelargonic acid:	244 mg
caprylic acid:	45 mg
heptanoic acid:	13 mg
azelaic acid:	212 mg
suberic acid:	24 mg
pimelic acid:	18 mg

15 The selectivity for azelaic acid is 82 %.

The selectivity for pelargonic acid is 79 %.

Example 3:

In this example the oxidative scission of oleic acid is performed in the presence of formic acid.

867 mg of oleic acid (3.07 mmol) and 5 g of formic acid are charged into a 50-ml three-necked round bottom flask fitted with a mechanical stirrer, a thermometer and a reflux device.

- 5 797 mg of an aqueous solution of 30% strength aqueous hydrogen peroxide (7 mmol) are then added and the reaction mixture is heated to 40°C for 2 hours.

A mixture containing 39 g of a 49% strength aqueous solution of nitric acid, 222 mg of ammonium
10 metavanadate and 100 mg of sodium nitrite is then added directly to the reaction mixture. The reaction mixture is then kept at 60°C for 6 hours.

The reaction mixture is then cooled, neutralized to pH = 2.3 with a 36% strength aqueous solution of
15 sodium hydroxide, diluted to 1 litre and analysed by capillary electrophoresis.

The results obtained are the following:

pelargonic acid:	247 mg
caprylic acid:	15 mg
heptanoic acid:	11 mg
azelaic acid:	284 mg
suberic acid:	24 mg
pimelic acid:	4 mg

The selectivity for pelargonic acid is 90 %.

The selectivity for azelaic acid is 90 %.

Example 4:

In this example the oxidative scission of erucic acid is performed in the presence of formic acid.

1.21 g of erucic acid (3.57 mmol), 0.36 g of
 5 formic acid and 0.8 g of 30% strength aqueous hydrogen peroxide (7.05 mmol) are charged into a stirred reactor fitted with a condenser and a temperature probe; the reaction mixture is then heated to 80°C for 7 h.

13.4 g of a 55% strength aqueous solution of
 10 nitric acid, 70 mg of sodium nitrite and 133 mg of ammonium metavanadate are then added directly to the reaction mixture. The reaction mixture is then kept at 61°C for 5 h 30 min.

The reaction mixture is then cooled, and
 15 neutralized to pH = 2.3 with a 36% strength aqueous sodium hydroxide solution. The reaction mixture is then esterified and analysed by gas phase chromatography.

The results obtained are the following:

dimethyl brassylate:	465 mg
dimethyl dodecanedioate:	109 mg
dimethyl suberate:	1 mg
methyl pelargonate:	291 mg
methyl caprylate:	52 mg
methyl heptanoate:	2 mg

The selectivity for brassylic acid is 80 %.

20 The selectivity for pelargonic acid is 83 %.

Example 5:

In this example the oxidative scission of petroselenic acid is performed in the presence of formic acid.

0.99g of petroselenic acid (3.51 mmol), 0.37g of formic acid and 0.8g of 30% strength aqueous hydrogen peroxide (7.05 mmol) are charged into a stirred reactor fitted with a condenser and a temperature probe; the reaction mixture is then heated to 80°C for 7 h.

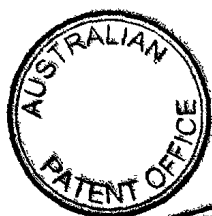
13.4g of a 55% strength aqueous solution of nitric acid, 70mg of sodium nitrite and 133mg of ammonium metavanadate are then added directly to the reaction mixture. The reaction mixture is then kept at 61°C for 5 h 30 min. The reaction mixture is then cooled, and neutralized to pH = 2.3 with a 36% strength aqueous sodium hydroxide solution. The reaction mixture is then esterified and analysed by gas phase chromatography.

The results obtained are the following:

15	dimethyl adipate:	287 mg
	dimethyl glutarate:	40mg
	methyl laurate:	400mg
	methyl undecanoate:	65mg
	methyl decanoate:	4mg

20 The selectivity for adipic acid is 80%.

The selectivity for lauric acid is 78%.



Example 6:

In this example the oxidative scission of methyl oleate is performed in the presence of formic acid.

1.049 g of methyl oleate (3.54 mmol), 0.36 g of
 5 formic acid and 0.8 g of 30% strength aqueous hydrogen peroxide (7.05 mmol) are charged into a stirred reactor fitted with a condenser and a temperature probe; the reaction mixture is then heated to 80°C for 7 h.

13.4 g of a 55% strength aqueous solution of
 10 nitric acid, 70 mg of sodium nitrite and 133 mg of ammonium metavanadate are then added directly to the reaction mixture. The reaction mixture is then kept at 61°C for 5 h 30 min. The reaction mixture is then cooled, and neutralized to pH = 2.3 with a 36% strength
 15 aqueous sodium hydroxide solution. The reaction mixture is then esterified and analysed by gas phase chromatography.

The results obtained are the following:

dimethyl azelate:	495 mg
dimethyl suberate:	51 mg
dimethyl pimelate:	4 mg
methyl pelargonate:	384 mg
methyl caprylate:	39 mg
methyl heptanoate:	5 mg

The selectivity for azelaic acid is 89 %.

20 The selectivity for pelargonic acid is 89 %.

Example 7 :

5 In this example the oxidative scission of oleic acid is performed in the presence of hydrogen peroxide alone.

1.01 g of oleic acid (3.59 mmol) and 0.8 g of 30% strength aqueous hydrogen peroxide (7.05 mmol) are charged into a stirred reactor fitted with a condenser

and a temperature probe; the reaction mixture is then heated to 80°C for 7 h.

13.4 g of a 55% strength aqueous solution of nitric acid, 70 mg of sodium nitrite and 133 mg of ammonium metavanadate are then added directly to the
10 reaction mixture. The reaction mixture is then kept at 61°C for 5 h. The reaction mixture is then cooled and neutralized to pH = 2.3 with a 36% strength aqueous sodium hydroxide solution. The reaction mixture is then esterified and analysed by gas phase chromatography.

15 The results obtained are the following:

dimethyl azelate:	76 mg
dimethyl suberate:	45 mg
dimethyl pimelate:	8 mg

dimethyl adipate: 24 mg

methyl pelargonate: 119 mg

methyl caprylate: 41 mg

methyl heptanoate: 6 mg

The selectivity for azelaic acid is 50 %.

The selectivity for pelargonic acid is 68 %.

Example 8:

5 In this example the oxidative scission of oleic acid is performed in the presence of sulfuric acid.

1.01 g of oleic acid (3.59 mmol), 0.12 of 98% strength sulphuric acid and 0.8 g of 30% strength aqueous hydrogen peroxide (7.05 mmol) are charged into a stirred reactor fitted with a condenser and a temperature probe; the reaction mixture is then heated to 80°C for 7 h.

10 13.4 g of a 55% strength aqueous solution of nitric acid, 70 mg of sodium nitrite and 133 mg of ammonium metavanadate are then added directly to the reaction mixture. The reaction mixture is then kept at 61°C for 5 h. The reaction mixture is then cooled and

neutralized to pH = 2.3 with a 36% strength aqueous sodium hydroxide solution. The reaction mixture is then esterified and analysed by gas phase chromatography.

5 The results obtained are the following:

dimethyl azelate:	316 mg
dimethyl suberate:	136 mg
dimethyl pimelate:	13 mg
dimethyl adipate:	6 mg
methyl pelargonate:	238 mg
methyl caprylate:	91 mg
methyl heptanoate:	7 mg

The selectivity for azelaic acid is 71 %.

The selectivity for pelargonic acid is 60 %.

Example 9:

10 In this example the oxidative scission of oleic acid is performed in the presence of tungstic acid.

1.0 g of oleic acid (3.54 mmol), 0.206 g of tungstic acid and 0.8 g of 30% strength aqueous hydrogen peroxide (7.05 mmol) are charged into a stirred reactor fitted with a condenser and a temperature probe; the reaction mixture is then heated

to 80°C for 5 h.

13.4 g of a 55% strength aqueous solution of
5 nitric acid, 70 mg of sodium nitrite and 133 mg of
ammonium metavanadate are then added directly to the
reaction mixture. The reaction mixture is then kept at
61°C for 6 h.

The reaction mixture is then cooled and
10 neutralized to pH = 2.3 with a 36% strength aqueous
sodium hydroxide solution. The reaction mixture is then
esterified and analysed by gas phase chromatography.

The results obtained are the following:

dimethyl azelate:	544 mg
dimethyl suberate:	82 mg
dimethyl pimelate:	8 mg
dimethyl adipate:	5 mg
methyl pelargonate:	416 mg
methyl caprylate:	58 mg
methyl heptanoate:	4 mg

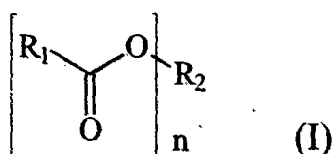
The selectivity for azelaic acid is 84 %.

The selectivity for pelargonic acid is 86 %.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for preparation of mono- and dicarboxylic acids from unsaturated fatty acids and/or their derivatives, comprising the following stages:

- a stage which consists in oxidizing an unsaturated fatty acid in the form of acid and/or of ester containing at least one double bond corresponding to the formula (I):



in which:

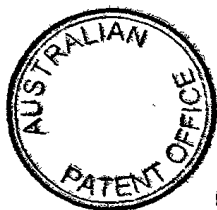
- n is a number equal to 1, 2 or 3,
- R_1 denotes a linear or branched alkenyl or alkadienyl radical containing from 4 to 40 carbon atoms,
- R_2 may take the following meanings:
 - if $n = 1$, R_2 denotes a hydrogen atom or an alkyl radical, optionally carrying one or more hydroxyl groups,
 - if $n = 2$, R_2 denotes an alkylene or alkenylene radical, optionally carrying one or more hydroxyl groups,
 - if $n = 3$, R_2 denotes an alkyl radical containing 3 carbon atoms, using hydrogen peroxide, in the presence of a metal oxide or of a carboxylic acid optionally used in combination with a ruthenium-based catalyst,
- a stage which consists in reacting the reaction mixture originating from the preceding stage with nitric acid in the presence of a vanadium-based catalyst, optionally used in combination with a cocatalyst, and then
- a stage of recovery of the mono- and dicarboxylic acids.



2. A process according to claim 1, wherein, when n is 1, and R_2 is an alkyl radical, the alkyl radical contains from 1 to 6 carbon atoms.
3. A process according to claim 1, wherein, when $n = 2$ and R_2 is an alkylene or alkenylene radical, that radical contains from 1 to 6 carbon atoms.
- 5 4. A process according to any one of Claims 1 to 3, wherein the unsaturated fatty acid corresponds to the formula (I) in which R_1 denotes an alkenyl radical containing from 6 to 22 carbon atoms and containing from 1 to 5 double bonds, and R_2 denotes a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms optionally carrying from 1 to 2 hydroxyl groups where $n = 1$, a diethylene or propylene radical optionally carrying a
10 hydroxyl group where $n = 2$ or a 1,2,3-propanetriyl radical where $n = 3$.
5. A process according to claim 4, wherein the alkenyl radical contains 1 to 3 double bonds.
6. A process according to any one of claims 1 to 5, wherein the starting substrate is chosen from:
15
 - unsaturated fatty acids containing only one double bond, unsaturated fatty acids containing two double bonds, unsaturated fatty acids containing three double bonds, unsaturated fatty acids containing more than four double bonds, and unsaturated fatty acids carrying a hydroxyl group, and mixtures thereof,
 - oils and fats of animal origin,
 - 20 - oils of vegetable origin,
 - the esters corresponding to the abovementioned fatty acids,



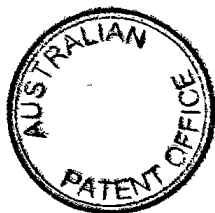
7. A process according to claim 6, wherein the unsaturated fatty acid containing only one double bond is selected from linderic acid, myristoleic acid, palmitoleic acid, oleic acid, petroselenic acid, doeglic acid, gadoleic acid and erucic acid.
8. A process according to claim 6, wherein the unsaturated fatty acid containing two
5 double bonds is linoleic acid.
9. A process according to claim 6, wherein the unsaturated fatty acid containing three double bonds is linolenic acid.
10. A process according to claim 6, wherein the unsaturated fatty acid containing more than four double bonds is selected from isanic acid, steardonic acid, arachidonic acid
10 and chypanodonic acid.
11. A process according to claim 6, wherein the unsaturated fatty acid carrying a hydroxyl group is ricinoleic acid.
12. A process according to claim 6, wherein the oil and fats of animal origin are selected from sperm whale oil, dolphin oil, whale oil, seal oil, sardine oil, herring oil,
15 dogfish oil and cod liver oil, neat's foot oil and beef, pork, horse and mutton fats (tallows).
13. A process according to claim 6, wherein the oils of vegetable origin are selected from rapeseed oil, sunflower oil, groundnut oil, olive oil, nut oil, corn oil, soya oil, linseed oil, hemp oil, grapeseed oil, copra oil, palm oil, cottonseed oil, babassu oil,
20 jojoba oil, sesame oil and castor oil.
14. A process according to claim 6, where the esters are methyl, ethyl or propyl esters.
15. A process according to claim 6, wherein the esters are products of methanolysis.



16. A process according to claim 15, where the products of methanolysis are products of methanolysis of the oils.
17. A process according to claim 15 or 16, wherein the products of methanolysis are products of methanolysis of rapeseed oils.
- 5 18. A process according to any one of claims 1 to 17, wherein the starting substrate is palmitoleic acid, oleic acid, petroselenic acid, erucic acid, linoleic acid, linolenic acid, ricinoleic acid, rapeseed oil, sunflower oil, soya oil, linseed oil, castor oil.
19. A process according to claim 18, wherein the starting substrate is oleic acid, rapeseed oil, sunflower oil or soya oil.
- 10 20. A process according to any one of claims 1 to 19, wherein the quantity of hydrogen peroxide used is a quantity equal to the stoichiometry or a slight excess ranging from 0 to 50%.
21. A process according to claim 20, where the quantity is between 1 and 20%.
22. A process according to any one of claims 1 to 21, wherein the hydrogen peroxide
15 is used in combination with a carboxylic acid.
23. A process according to claim 22, wherein the carboxylic acid corresponds to the general formula (II):



- in the said formula (II), R_3 denotes a hydrocarbon radical containing from 1 to 22 carbon
20 atoms.
24. A process according to claim 23, wherein the hydrocarbon radical is a linear or branched, saturated acyclic aliphatic radical or a monocyclic or polycyclic saturated cycloaliphatic radical.



25. A process according to any one of claims 22 to 24, wherein the carboxylic acid is a saturated aliphatic carboxylic acid, or an acid formed in the course of the reaction.
26. A process according to claim 25, wherein the carboxylic acid is formic acid or acetic acid.
- 5 27. A process according to claim 25, where the acid formed is pelargonic acid, azelaic acid or stearic acid.
28. A process according to any one of claims 22 to 27, wherein the quantity of carboxylic acid which is used is such that the molar ratio of hydrogen peroxide to the carboxylic acid varies between 10 and 500%.
- 10 29. A process according to claim 28, wherein the ratio varies between 10 and 40%.
30. A process according to any one of claims 22 to 29, wherein a ruthenium-based catalyst is added.
31. A process according to any one of claims 22 to 30, wherein a ruthenium-based catalyst is used and is chosen from ruthenium(III) chloride, ruthenium(IV) chloride,
- 15 ruthenium pentafluoride, ruthenium(II) oxide, ruthenium(IV) oxide, ammoniated ruthenium oxychloride $\text{Ru}_2(\text{OH})_2\text{Cl}_4 \cdot 7\text{NH}_3 \cdot 5\text{H}_2\text{O}$ and ruthenium acetate.
32. A process according to either of claims 30 and 31, wherein the quantity of the ruthenium-based catalyst, expressed as the weight ratio of hydrogen peroxide to the catalyst is between 1 and 35%.
- 20 33. A process according to claim 32, wherein the quantity is between 3 and 10%.
34. A process according to any one of claims 1 to 21, wherein the hydrogen peroxide is used in combination with a catalyst based on a metal of group VIa of the Periodic

Classification of the elements.



35. A process according to claim 34, wherein the catalyst is a tungsten- and/or molybdenum-based catalyst.

36. A process according to any one of claims 1 to 21, 34 or 35, wherein the catalyst is chosen from tungstic acid, phosphotungstic acid, molybdic acid, phosphomolybdic acid
5 or their precursors.

37. A process according to any one of claims 1 to 21, 34 to 36, wherein the quantity of tungsten- and/or molybdenum-based catalyst used, expressed as the weight ratio of hydrogen peroxide to the catalyst, is between 1 and 35%.

38. A process according to claim 37, wherein the ratio is between 3 and 10%.

10 39. A process according to any one of claims 36 to 38, wherein a strong acid is added.

40. A process according to claim 39, wherein the strong acid is nitric acid, sulphuric acid or phosphoric acid.

41. A process according to any one of claims 1 to 40, wherein the temperature of the first oxidation stage is between 30 and 100°C.

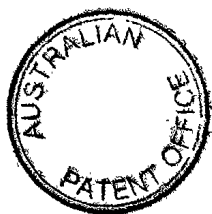
15 42. A process according to claim 41, wherein the temperature is between 60° and 100°C.

43. A process according to any one of claims 1 to 42, wherein the quantity of nitric acid used in the second stage represents from 2 to 50 times the weight of the starting substrate.

20 44. A process according to claim 43, where the nitric acid is from 4 to 10 times the weight of the starting substrate.



45. A process according to claim 43 or 44, wherein a source of NO^+ is added, chosen from nitrogen dioxide NO_2 , nitrogen trioxide N_2O_3 , nitrogen peroxide N_2O_4 , nitrogen oxide NO , nitrous acid, a nitrosylsulphate or nitrosylsulphuric acid, or a nitrous salt.
46. A process according to claim 45, wherein the nitrous salt is an alkali metal salt.
- 5 47. A process according to claim 45 or 46, wherein the nitrous salt is a sodium salt.
48. A process according to any one of claims 43 to 47, wherein the vanadium-based catalyst is chosen from:
- vanadium halides,
 - vanadium oxides,
 - 10 - vanadium oxyhalides,
 - vanadium sulphate,
 - vanadyl sulphate,
 - alkali metal or ammonium vanadates in the ortho, meta or pyro form,
 - vanadyl acetylacetonate.
- 15 49. A process according to claim 48, wherein the vanadium halides are selected from vanadium tri-, tetra- or pentafluoride, vanadium di-, tri- or tetrachloride or vanadium tribromide.
50. A process according to claim 48, wherein the vanadium oxides are selected from vanadium oxide, vanadium dioxide, vanadium sesquioxide or vanadium pentoxide.
- 20 51. A process according to claim 48, wherein the vanadium oxyhalides are selected from vanadium oxydi- or trifluoride, vanadium oxymono-, di- or trichloride and vanadium oxymono-, di- or tribromide.



52. A process according to any one of claims 43 to 51, wherein the quantity of vanadium-based catalyst used, expressed as the weight ratio of the catalyst, expressed as HVO_3 , to nitric acid is between 0.001 and 1%.
53. A process according to claim 52, wherein the ratio is between 0.02 and 0.5%.
- 5 54. A process according to any one of claims 43 to 53, wherein a cocatalyst based on a metal of group VIIa and VIII of the Periodic Classification is added.
55. A process according to claim 54, wherein a catalyst based on manganese, iron, nickel, ruthenium and/or cobalt is added.
56. A process according to any one of claims 43 to 55, wherein the nitric oxidation
10 stage is performed in the presence of oxygen or a gas containing it.
57. A process according to claim 56, wherein the quantity of oxygen represents from 1 to 2 times the stoichiometric quantity when the starting substrate is an unsaturated fatty acid and from 5 to 8 times the stoichiometric quantity when the raw material is an oil or a fat.
- 15 58. A process according to any one of claims 43 to 57, wherein the reaction temperature in the second stage is chosen between 40°C and 100°C .
59. A process according to claim 58, wherein the temperature is chosen between 60°C and 90°C .
60. A process according to any one of claims 1 to 59 wherein a two-phase mixture is
20 obtained with an aqueous phase including the saturated dicarboxylic fatty acids, the nitric acid, the catalysts and cocatalysts, and an organic phase including essentially the saturated monocarboxylic fatty acids formed in the course of the reaction and optionally



those present initially, as well as the unsaturated fatty acids which have not reacted and in that the saturated mono- and dicarboxylic fatty acids obtained are separated.

61. A process for the preparation of mono- and dicarboxylic acids, substantially as herein described with reference to any one of the Examples.

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DATED this 12th day of October 1998

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10



ABSTRACT

The present invention relates to a process for the preparation of carboxylic acids from unsaturated fatty acids and/or their derivatives.

5 The process of the invention is characterized in that it comprises the following stages:

- 10 - a stage which consists in oxidizing an unsaturated fatty acid in the form of acid and/or of ester using hydrogen peroxide, in the presence of a metal oxide or of a carboxylic acid optionally used in combination with a ruthenium-based catalyst,
- 15 - a stage which consists in reacting the reaction mixture originating from the preceding stage with nitric acid in the presence of a vanadium-based catalyst, optionally used in combination with a cocatalyst, and then
- 20 - a stage of recovery of the mono- and dicarboxylic acids.

It is particularly well suited for the preparation of saturated mono- and dicarboxylic acids obtained from unsaturated fatty acids such as oleic acid or from oils and fats.