(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 January 2002 (03.01.2002)

PCT

(10) International Publication Number
WO 02/00592 A1

(51) International Patent Classification[7]: C07C 67/31, 69/708, 67/03, 231/02, C10M 105/34, A61K 7/00, A23L 1/00

(21) International Application Number: PCT/BE01/00111

(22) International Filing Date: 27 June 2001 (27.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00305404.6 27 June 2000 (27.06.2000) EP

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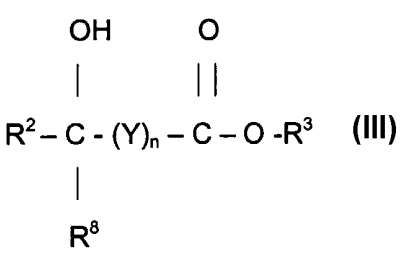
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EC, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PRODUCTION OF ALKOXYCARBOXYLIC ESTERS AS FATTY ACID ALTERNATIVES



(57) Abstract: The invention relates to a process for the production of an ester of an alkoxycarboxylic acid characterised in that the process comprises the step of reacting (a) a first unsaturated compound comprising at least one olefin group a 2-24 carbon atoms with (b) a hydroxy acid ester compound corresponding to the formula (III) in which Y denotes CR^4R^5 - or CR^4R^5 - CR^6R^7; R^2, R^3, R^4, R^5, R^6, R^7, R^8 denote C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, aryl, C_7-C_{20} aralkyl, C_7-C_{20} alkylaryl and may contain further substituents, the substituent being any organic group and/or any organic group containing one or more hetero-atoms selected from any of B, Si, N, P, O, or S atom or a halogen atom. R^2, R^3, R^4, R^5, R^6, R^7, R^8 can additionally denote hydrogen n = 0 or 1, in the presence of a heterogeneous acid catalyst or a homogeneous superacid catalyst, wherein the compounds (a) and (b) may be independently of each other, linear or branched, and/or substituted or non-substituted.

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PRODUCTION OF ALKOXYCARBOXYLIC ESTERS AS FATTY ACID ALTERNATIVES

Background of the invention.

The present invention relates to a process for the production of an alkoxycarboxylic acid and an ester of an alkoxycarboxylic acid.

The alkoxycarboxylic acid as well as the ester obtainable with the process of this invention is a useful alternative for natural fatty acids. C_8-C_{10} fatty acid fractions find wide application in the production of fatty acid derivatives for use as lubricants, in cosmetic compositions or in other industrial applications where their specific properties of good oxidation and cold stability are desirable. C_8-C_{10} fatty acid fractions are mainly to be found in coconut oil or palm kernel oil. However those C_8-C_{10} fatty acid fractions are rather scarce in nature (see table 1 below), which in turn involves a shortage of the availability of the C_8-C_{10} fraction and undesirably high market prices.

In view of the properties required in applications in oleochemistry, preferred fatty acids are the saturated fatty acids which show a good cold stability (low melting point) and good oxidation stability. However, in practise only few natural fatty acids satisfy these two criteria. Fatty acids satisfying these criteria are those present in the C_8-C_{10} fraction of for example coconut oil and palm kernel oil. The physical properties of some of these fatty acids are shown in Table 1.

Table 1

	Melting point °C	**Content in coconut oil / %**	**Content in palm kernel oil / %**
C8 (caprylic acid)	16.0	8	3
C10 (capric acid)	31.6	6	3
C12 (lauric acid)	44.2		

It can immediately be seen from table 1 that caprylic and capric acid at ambient temperature will usually be in the molten state, whereas lauric acid however will already be solid.

To overcome the limited availability and high market prices of the naturally occurring C_8-C_{10} fatty acid fractions, synthetic alternatives have been developed, such as for example esters of ether alcohols. At present the production methods for these synthetic alternatives are still too expensive or environmentally unsound. A well-known method for producing the ester of an alcohol ether is the alkoxy-mercuration/demercuration reaction. This method is a two-stage process in which an alkene is reacted with an alcohol in the presence of a mercury-containing catalyst, for example mercuric trifluoroacetate. In the first stage the alcohol and mercury species react with the alkene to bond with the alkene carbon atoms. In the second stage a demercuration of the thus obtained product is carried out using, for example sodium borohydride. The release of elemental mercury occurring in this demercuration step is however unacceptable on an industrial scale, as elemental mercury is hazardous to the environment and expensive to remove. Moreover, the presence of any remaining mercury in the reaction product is to be avoided when using the alcohol ether ester in cosmetic applications for example.

Description of the prior art.

In EP-A-632.011 a method for the production of an alkoxycarboxylic acid ester is disclosed, by reaction of a hydroxycarboxylic acid ester with an alcohol. The reaction is catalysed by a heterogeneous catalyst, for example a faujasite zeolite, ZSM-5, X-type, Y-type or L-type zeolite, alumino-phosphate AlPO's or a silicoalumonphosphate (SAPO's). Preferred temperatures for carrying out the reaction are between 180-320°C. However, at these temperatures transesterification reactions have been found to take place thus leading to undesired side products.

In Gluchowski et al., J. Medicinal Chemistry, 1991, vol. 34 (1), p. 396 a method for synthesising 2-tert-butoxyacetic acid is disclosed. In a first step isobutylene is caused to react with n-butylglycolate in the presence of concentrated sulfuric acid, using chloroform as a solvent. The reaction is carried out at room temperature. After quenching the reaction mixture the ether reaction

product is extracted from the reaction mixture and isolated by distillation. Following this the ether reaction product is subjected to hydrolysis in the presence of potassium carbonate in a second step, using methanol as a solvent. This known synthesis method however involves several intermediate isolation and purification steps, as a consequence of which the yield of the 2-tert-butoxyacetic acid is too low. Moreover, the purity of the product does not satisfy the current needs. There is thus a need to provide a process with improved yields of the alkoxycarboxylic acid esters.

Brief description of the invention.

It is an object of the present invention to provide a process with which the alkoxycarboxylic acid and the ester of the alkoxycarboxylic acid may be obtained at improved purity and better yield.

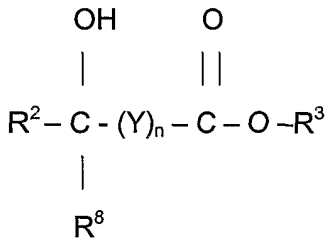
This is achieved with the present invention with the technical features of the characterising part of the first claim.

The process of the present invention for the production of an ester of an alkoxycarboxylic acid comprises the step of reacting:

(a) a first compound comprising at least one olefin group and having from 2-24 carbon atoms, the first compound may be linear or branched, and contain one or more substituents.

with

(b) a hydroxy acid or an ester of a hydroxy acid compound corresponding to the formula (III)



in which

Y denotes CR^4R^5 or CR^4R^5 - CR^6R^7

R^2, R^3, R^4, R^5, R^6, R^7, R^8 denote C_1-C_{20} alkyl linear or branched, saturated or containing one or more unsaturated bonds, C_3-C_8 cycloalkyl saturated or

unsaturated, aryl, C_7-C_{20} aralkyl, C_7-C_{20} alkylaryl, and may contain further substituents, for example any organic group and/or one or more hetero-atoms. Hetero atoms may be selected from any of groups IIIA, IVA, VA, VIA or VIIA of the Periodic Table, in particular a B, Si, N, P, O, or S atom or a halogen atom.

and

R^2, R^3, R^4, R^5, R^6, R^7, R^8 can additionally denote hydrogen

$n = 0$ or 1

in the presence of a heterogeneous acid catalyst or a homogeneous superacid catalyst, wherein the compounds (a) and (b) may be independently of each other, linear or branched, substituted or non-substituted.

According to a preferred embodiment of this invention, compound (b) is a hydroxy acid ester compound having from 2-8 carbon atoms, the carbon atoms of the ester moiety excluded. A hydroxy acid ester is preferred over the hydroxy acid, because in this way polymerisation of the hydroxy acid may be avoided.

With the process of the present invention alkoxycarboxylic acids and esters of alkoxycarboxylic acids, in particular methyl or butyl esters of the alkoxycarboxylic acids, may be synthesised the properties of which are very close to those of the esters of the C_8-C_{10} fatty acids. The process of this invention provides an improved yield of the desired ester and a better selectivity towards the desired ester as compared to the prior art. The use of a shape selective zeolite as a catalyst allows limiting the formation of undesired side products. Moreover, the process has been found to be more environmentally friendly than the known synthetic routes.

The compounds (a) and (b) may be linear or branched or substituted or unsubstituted, as discussed above. The substituents are not particularly limited, provided that the final products have the desired properties, and may comprise any organic group and/or one or more atoms from any of groups IIIA, IVA, VA, VIA or VIIA of the Periodic Table, such as a B, Si, N, P, O, or S atom or a halogen atom (e.g. F, Cl, Br or I).

When the substituent comprises an organic group, the organic group preferably is a hydrocarbon group. The hydrocarbon group may

comprise a straight chain, a branched chain or a cyclic group. The hydrocarbon group of compound (a) or (b) may comprise independently from each other an aliphatic or an aromatic group. Also independently, the hydrocarbon group of compound (a) or (b) may comprise independently from each other, a saturated or unsaturated group.

When the hydrocarbon group comprises an unsaturated group, it may comprise one or more alkene functionalities and/or one or more alkyne functionalities. When the hydrocarbon group comprises a straight or branched chain group, it may comprise one or more , secondary and/or tertiary alkyl groups. When the hydrocarbon group comprises a cyclic group it may comprise an aromatic ring, an aliphatic ring, a heterocyclic group, and/or fused ring derivatives of these groups. The cyclic group may thus comprise a benzene, naphthalene, anthracene, indene, fluorene, pyridine, quinoline, thiophene, benzothiophene, furan, benzofuran, pyrrole, indole, imidazole, thiazole, and/or an oxazole group, as well as regioisomers of the above groups.

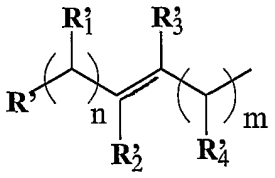
The number of carbon atoms in the hydrocarbon group is not especially limited, but preferably the hydrocarbon group comprises from 1-22 C atoms. The hydrocarbon group may thus be a lower hydrocarbon (1-6 C atoms) or a higher hydrocarbon (7 C atoms or more, e.g. 7-22 C atoms). The number of atoms in the ring of the cyclic group is not especially limited, but preferably the ring of the cyclic group comprises from 3-10 atoms, such as 3, 4, 5, 6 or 7 atoms.

Preferably however component (a) is free of substituents containing unsaturated alkyl groups and contains only one single double bond to avoid the formation of undesired side products.

The groups comprising heteroatoms described above, as well as any of the other groups defined above, preferably comprise one or more heteroatoms from the group of B, Si, N, P, O, or S atom or a halogen atom (e.g. F, Cl, Br or I). In addition, any substituent may comprise a combination of two or more of the substituents and/or functional groups defined above.

In a preferred embodiment of the present invention, the process comprises reacting:

(a) a compound of formula (I):

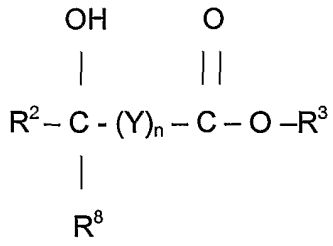


(I)

in which n is an integer of 0-22; m is an integer of 0-22 provided that n+m is 22 or less; preferably R' is H; and R'^1, R'^2, R'^3 and R'^4 are independently selected from H, halogen, and a substituent comprising a carbon atom, such as a substituent as defined above;

with

(b) a compound of formula (II):



(II)

in which

Y denotes CR^4R^5 or CR^4R^5 - CR^6R^7

R^2, R^3, R^4, R^5, R^6, R^7, R^8 denote C_1-C_{20} alkyl linear or branched, saturated or containing one or more unsaturated bonds, C_3-C_8 cycloalkyl saturated or unsaturated, aryl, C_7-C_{20} aralkyl, C_7-C_{20} alkylaryl, and may contain further substituents, for example any organic group and/or one or more heteroatoms from the group of B, Si, N, P, O, or S atom or a halogen atom

and

R^2, R^3, R^4, R^5, R^6, R^7, R^8 can additionally denote hydrogen

n = 0 or 1

It is particularly preferred that the R^3 group is an alkyl group having from 1-8 carbon atoms, for example an ethyl, propyl, butyl, t-butyl or iso-butyl residue. Most preferably R^3 is a methyl- or butyl- group.

In preferred embodiments of the invention, the compounds (a) and (b) are non-substituted and are linear. In that case R'1, R'2, R'3, R'4 and R^8 are each H. Particularly preferred as compound (b) is methyl glycolate or butyl glycolate. Particularly preferred as compound (a) are C_2-C_{10} α-olefins such as ethene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene.

When the products of the present process are intended to replace C_8-C_{10} fatty acid fractions, the alkoxycarboxylic acid is preferably a compound comprising or derivatives of these fractions from 8-14 carbon atoms, excluding the carbon atoms of the ester moiety. However, the final product may have from 4-26 carbon atoms, if desired, excluding the carbon atoms of the ester moiety.

The catalyst used in the present process is a heterogeneous acid catalyst or may be a homogeneous superacid catalyst. Preferably the catalyst comprises a zeolite, an acid resin or a solid amorphous catalyst, such as silica-alumina. When the catalyst comprises a zeolite, the preferred zeolite is a Y-type zeolite. Superacids (solutions of strong acids in very acidic solvents) such as SbF_5 in HF (SbF_6^- in H_2F^+) and SbF_5 in HSO_3F ($FSO_3SbF_5^-$ + $H_2SO_3F^+$) or other superacids may also be used as catalysts if so desired.

The temperature of the present process is not especially limited, provided that the process proceeds to form the desired alkoxycarboxylic acid ester. However, preferably the compounds (a) and (b) are reacted at a temperature of from 100-240°C. More preferably the temperature employed is from 120-200°C

The present invention also relates to a process for transesterification to produce further esters, and/or production of a amide from the above mentioned alkoxycarboxylic acid ester.

Thus the present process may further comprise performing a transesterification step on the product ester of an alkoxycarboxylic acid, to produce a further ester of an alkoxycarboxylic acid. The present process

may also further comprise a step of forming an amide compound from the product ester of an alkoxycarboxylic acid. Preferably, the amide compound is a low melting point amide compound.

As discussed above, the present alkoxycarboxylic acid ester compounds, and their derivatives, have a wide variety of possible applications. In particular they may be used as a replacement for a natural fatty acid or its derivative in a composition. They may also be used to improve the cold stability of a composition. Typically applications of alkoxycarboxylic acid esters include their use as lubricants, in cosmetics compositions, as solvents or in compositions requiring good cold stability. The alkoxycarboxylic acid ester of this invention is for example suitable for use as a solvent in solvent compositions when replacing existing solvent compositions that are harmful to the environment.

The present invention will be further described by way of example only, with reference to the following specific embodiments.

EXAMPLES.

Example 1.

1 mole of methylglycolate was caused to react with 2 moles of 1-octene (1 mole excess) using 1 % zeolite CBV 720 from Zeolyst International as catalyst (CBV 720 is a Y-type zeolite with a SiO2/Al2O3 ratio of 30). The reaction was carried out at 130°C for 3 hours with a nitrogen pressure of 1.3 bar. The reaction product methyl(1-methylheptylloxy)acetate was separated from non-reacted methylglycolate and 1-octene by simple fractionation. In an industrial process these non-reacted reactants can be recycled. The molar yield of the alkoxycarboxylic acid methylester relative to the initial amount of methylglycolate was 27.2%.

Example 2.

Example 1 was repeated, except that a temperature of 120°C was used and Amberlyst 15 from Rohm & Haas was employed as catalyst (an acid resin). The molar yield of methylester of the alkoxycarboxylic acid relative to the initial amount of butylglycolate was 4.9%. It is clear that zeolites with strong acidity are the preferred catalysts for this reaction.

Example 1 was repeated in the presence of a generally known homogeneous acid catalyst, like paratoluenesulphonic acid. The yield of the methylester of the alkoxycarboxylic acid was negligible.

Example 3.

1 mole of n-butylglycolate was caused to react with 1.3 moles of 1-dodecene (30% mole excess) using 3.7 wt. % of a mixture of various zeolites as catalyst. The reaction was carried out at a pressure of 8 bar nitrogen pressure. N-butylglycolate is a generally available chemical commodity, which is often used as solvent. The reaction product butyl-(1-methyl-undecyloxyacetate was separated from the non-reacted butylglycolate and 1-dodecene by simple fractionation. The molar yields of the butylester of alkoxycarboxylic acid relative to the initial quantity of butylglycolate are given in the table below.

All CBV type zeolites were purchased from Zeolyst International. ZSM-5 was purchased from Degussa. The zeolites were calcined for 3 hours at 525°C before being added to the reaction mixture. The butylglycolate was purchased from Du Pont.

Zeolite	Type	SiO2/Al2O3 Ratio	Molar yield of alkoxycarboxylic acids (%)
CBV 500	Y	5.2	0.32
CBV 712	Y	12	13.0
CBV 720	Y	30	15.8
CBV 760	Y	60	14.7
CBV 780	Y	80	15.9
ZSM-5	silicalite	280	0.35

As can be seen from the table above, zeolite Y is a good catalyst for this reaction, on condition that the SiO2/Al2O3 ratio of the zeolite is > 5. Most probably this must be explained by the fact that the acid strength of active sites of a zeolite increases with increasing SiO2/Al2O3 ratio.

Silicalite turned out to be less favourable. This may probably be explained by the fact that the dimensions of the pores of the ZSM-5 porous system are too small to allow a sufficiently fast diffusion of the bulky reactants and reaction products.

The purity of the butylester of alkoxycarboxylic acid obtained in the above mentioned expertiments is 98.6% after fractionation, as determined by GLC. The cloud point of these butylesters of alkoxycarboxylic acids with 14 carbon atoms is –59°C. The cloud point of butylmyristate, which is the natural fatty acid ester equivalent, amounts to 0°C.

These examples demonstrate that esters of alkoxycarboxylic acids can be produced in large amounts, with generally available starting materials and catalysts, in a simple cost-effective reaction. The obtainable alkoxycarboxylic acid esters have better cold properties than their natural fatty acid ester equivalents.

Example 4.

In the following examples it will be demonstrated that esters which are obtained by subjecting the ester of the alkoxycarboxylic acid obtainable with the process of examples 1-3 to a transesterification reaction, have very good cold properties.

The butylester of the alkoxycarboxylic acid obtained in example 3 (purity 98.6%) were caused to react with trimethylolpropane or 2-ethylhexanol. These types of esters are widely used as lubricants or solvents. The transesterification reactions was carried out in the reaction conditions set out below.

4.1. Trimethylolpropane ester.

The butylester of the alkoxycarboxylic acids was charged to a glass reactor together with trimethylolpropane. The molar ratio of the alkoxycarboxylic acid ester to trimethylolpropane was 3 to 1. This ration was selected to ensure achieve complete esterification of the trimethylolpropane. As a catalyst use was made of 0.2 wt. % of dibutyltinoxyde is used. After heating the reactor for 1 hour at 193°C, butanol was distilled off at atmospheric conditions. To achieve virtually complete conversion of the butyl ester of the alkoxycarboxylic

acid, gradually a vacuum was build up in the reactor (final pressure 3 mbar). After completion of the reaction, the reaction product was filtered to remove the catalyst.

4.2. 2-ethylhexanol ester. Transesterification reaction.

The butylester of alkoxycarboxylic acid was charged to a glass reactor together with 2-ethylhexanol in a molar ratio of 1-1.3. To this mixture, 0.2 % of dibutyltinoxyde catalyst was added. The reactor was heated to 177°C for a period of 4 hours. Thereafter butanol and the excess 2-ethylhexanol were gradually distilled off by applying a vacuum to the reactor. The destillation residue was filtered to separate the catalyst from the reaction product.

In the table below, the cloud points of the C14 alkoxycarboxylic acid based esters are compared to their natural myristic acid equivalents:

	Cloud point (°C)	
	Myristic acid	C14 alkoxycarboxylic acid
Trimethylolpropane ester	21	-42
2-ethylhexanol ester	-22	< - 64

From this table it should be clear that esters based on alkoxycarboxylic acids have a superior cold stability compared to natural fatty acids.

Example 5.

Esters made from natural fatty acids have the advantage that they are readily biodegradable. As the biodegradability may be an important criterium in certain applications, the biodegradability of the butylesters of the alkoxycarboxylic acid of example 3 (98.6% purity) was assessed using the closed bottle test OECD 301D. The results below show that the alkoxycarboxylic acid esters obtainable with this invention are readily biodegradable.

% biodegradation = BOD x 100 / COD

After 5 days: 18%

After 15 days: 71%

After 28 days: 77%

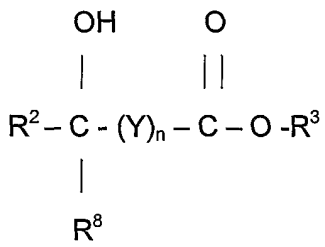
CLAIMS.

1. A process for the production of an ester of an alkoxycarboxylic acid characterised in that the process comprises the step of reacting

(a) a first unsaturated compound comprising at least one olefin group an 2-24 carbon atoms

with

(b) a hydroxy acid ester compound corresponding to the formula (III)



in which

Y denotes CR^4R^5 or CR^4R^5 - CR^6R^7

R^2, R^3, R^4, R^5, R^6, R^7, R^8 denote C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, aryl, C_7-C_{20} aralkyl, C_7-C_{20} alkylaryl and may contain further substituents, the substituent being any organic group and/or any organic group containing one or more hetero-atoms selected from any of B, Si, N, P, O, or S atom or a halogen atom.

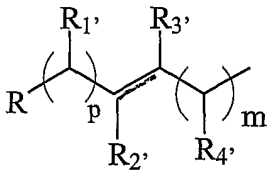
R^2, R^3, R^4, R^5, R^6, R^7, R^8 can additionally denote hydrogen

n = 0 or 1

in the presence of a heterogeneous acid catalyst or a homogeneous superacid catalyst, wherein the compounds (a) and (b) may be independently of each other, linear or branched, and/or substituted or non-substituted.

2. A process as claimed in claim 1, characterised in that compound (b) is a hydroxy acid ester having 2-8 carbon atoms, the carbon atoms of the ester moiety excluded.

3. A process as claimed in claim 1 or 2, characterised in that the first compound (a) corresponds to formula (I):



(I)

in which

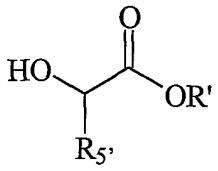
p is an integer of 0-22

m is an integer of 0-22 provided that p+m ≤ 22 ;

R is H

$R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$ are independently selected from H, halogen, a hydrocarbon group, which may be linear, branched, cyclic, aromatic, contain one or more unsaturations, contain one or more hetero-atoms and/or one or more substituents

and compound (b) corresponds to formula (II):



(II)

in which

R' is an alkyl group having 1-8 carbon atoms;

$R^{5'}$ comprises H, halogen, or a hydrocarbon group, which may be linear, branched, cyclic, aromatic, contain one or more unsaturations, contain one or more hetero-atoms and/or one or more substituents

4. A process as claimed in claim 3, characterised in that R' is a methyl- or butyl group.

5. A process as claimed in any one of claims 1-4, characterised in that $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$ and $R^{5'}$ are each H.

6. A process as claimed in any one of claims 1-5, characterised in that the ester of the alkoxycarboxylic acid is a compound

comprising from 8-12 carbon atoms, the carbon atoms of the ester moiety excluded.

7. A process as claimed in any one of claims 1-6, characterised in that the heterogeneous acid catalyst is selected from the group comprising zeolites, acid resins or solid amorphous catalysts.

8. A process as claimed in claim 7, characterised in that the zeolite is a Y-type zeolite.

9. A process as claimed in any one of claims 1-8, characterised in that the reaction is carried out at a temperature between 100-240°C.

10. A process as claimed in any one of claims 1-9, characterised in that process further comprises the step of performing a transesterification of the ester of the alkoxycarboxylic acid to produce a further ester of an alkoxycarboxylic acid.

11. A process as claimed in any of claims 1-9, characterised in that the ester of the alkoxycarboxylic acid is converted into a amide compound.

12. A process as claimed in claim 11, characterised in that the amide compound is a amide with low melting point.

13. Use of an ester of an alkoxycarboxylic acid, or a amide of an alkoxycarboxylic acid, obtainable according to a process as defined in any preceding claim, as a replacement for a natural fatty acid or its derivative in a composition.

14. Use of an ester of an alkoxycarboxylic acid, or a amide of an alkoxycarboxylic acid, obtainable according to a process as defined in any of claims 1-12, to improve the cold stability of a composition.

15. Use of an ester of an alkoxycarboxylic acid, or a amide of an alkoxycarboxylic acid, obtainable according to a process as defined in any of claims 1-12, as a lubricant, in a cosmetics composition, as a solvent, or in a composition requiring good cold stability and biodegradability.

16. A lubricant composition comprising an ester of an alkoxycarboxylic acid obtainable with the process of any one of claims 1-12.

17. A cosmetic composition comprising an ester of an alkoxycarboxylic acid obtainable with the process of any one of claims 1-12.

18. A solvent composition comprising an ester of an alkoxycarboxylic acid obtainable with the process of any one of claims 1-12.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BE 01/00111

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C67/31 C07C69/708 C07C67/03 C07C231/02 C10M105/34
A61K7/00 A23L1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C10M A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 411 409 A (BASF) 6 February 1991 (1991-02-06) page 5, line 42 - line 47; claims; examples ---	15,16,18
X	DATABASE WPI Section Ch, Week 9550 Derwent Publications Ltd., London, GB; Class A41, AN 1995-390250 XP002183524 & JP 07 267900 A (NITTO CHEM IN), 17 October 1995 (1995-10-17) abstract --- -/--	15,17,18

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2001	05/12/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Wright, M

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE WPI Section Ch, Week 9927 Derwent Publications Ltd., London, GB; Class B07, AN 1999-323869 XP002183525 & JP 11 116994 A (KYOWA YUKA), 27 April 1999 (1999-04-27) abstract	15,18
X	US 3 770 808 A (E. T. MARQUIS) 6 November 1973 (1973-11-06) the whole document	14-16
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