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(71) Applicant: L'OREAL [FR/FR]; 14, rue Royale, 75008 Paris (FR).

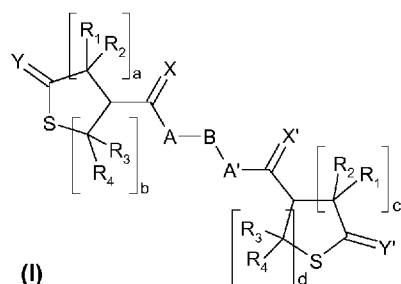
(72) Inventor: BLAISE, Christian; 1, ave Eugène Schueller, BP22, 93601 Aulnay-sous-Bois (FR).

(74) Agent: RIVIERE, François; D.I.P.I., 9 rue Pierre Dreyfus, 92110 Clichy (FR).

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(54) Title: COMPOSITION COMPRISING BISTHIOLACTONES AND PROCESS FOR TREATING KERATIN MATERIALS USING SAME



(57) Abstract: The present invention relates to i) a process for treating keratin materials, in particular human keratin fibres, comprising the application of a composition comprising at least one bithiolactone of formula (I), in particular for shaping keratin fibres and/or straightening/relaxing, ii) a composition comprising the bithiolactone(s) of formula (I), iii) novel bithiolactones of formula (I), iv) a process for preparing the novel bithiolactones of formula (I), and v) the use of said bithiolactones in cosmetics. In which formula (I), R₁, R₂, R₃, R₄, X, X', Y, Y', A, A', B, a, b, c, and d are as defined in the description.

COMPOSITION COMPRISING BISTHIOLACTONES AND PROCESS FOR TREATING KERATIN MATERIALS USING SAME

5 The present invention relates to i) a process for treating keratin materials, in particular human keratin fibres, comprising the application of a composition comprising at least one particular bithiolactone, in particular for shaping keratin fibres and/or straightening/relaxing, ii) a composition comprising the particular bithiolactone(s), iii) and novel bithiolactones, iv) a process for preparing the novel bithiolactones, and v) the use of said bithiolactones in cosmetics.

10 In the hair field, consumers wish to have available compositions which make it possible to introduce a temporary change to their head of hair, while targeting good shape retention of the effect produced. In general, it is desired for the change to withstand shampooing for at least fifteen days or even more, depending on the nature of said change.

15 Heat treatments are generally used to modify the shape of the head of hair in a long-lasting manner. These treatments allow a visual modification of the appearance of the hairstyle, combining a decrease in the degree of frizziness, a reduction in overall volume of the head of hair, a decrease in little curls, a gain in manageability, a straighter overall appearance, a substantial gain in sheen, and a resistance to humidity and to heat in order to maintain the hairstyle throughout the day.

20 Moreover, this type of treatment has the advantage of facilitating the daily maintenance of the head of hair, with the use of fewer care products, in particular rinse-out care products such as conditioners or masks, or leave-on care products such as sera, care creams or balms, or taming mousses. Drying of the hair is facilitated, with a much shortened blow-drying time and a decrease in the daily use of flat tongs, in terms both of time and intensity. This thus makes it possible to limit the risks of damaging the hair through combined factors of mechanical and thermal stress.

25 Several techniques are combined with these heat treatments. A first technique is based on the use of compositions based on thiol-based reducing agents. These techniques require strict adherence to the application conditions recommended by the suppliers, in particular in terms of amounts and leave-on time. In addition, they may be contraindicated on hair that is too sensitized and may not be compatible with the same-day application of other treatments, such as dyeing or bleaching operations. Moreover, they have an unpleasant smell.

35 Another technique is based on the use of compositions based on formol (or formaldehyde) and derivatives thereof. These treatments have the particularity of being robust, perfectly compatible with all the other conventional hair treatments, such as the thiol-based straightening operations previously mentioned, alkaline relaxing operations,

dyeing or bleaching operations of all types, carried out before or after. They provide the hair with excellent manageability, a very bright sheen and easy daily care. However, in the event of repeated applications, further damage to the hair occurs, which can lead to breaking of the hairs. Furthermore, for toxicological reasons, the use of some of these compounds is now prohibited and/or regulated. It is therefore increasingly sought to avoid the use of such substances, which may prove to be aggressive to the hair and other keratin materials.

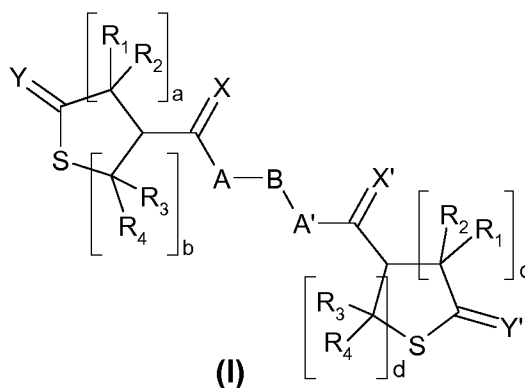
Another technique is based on the use of compositions based on acids, and quite particularly on the use of glyoxylic acid. Patent application WO 2011/104 282 thus proposed a novel process for semi-permanently straightening the hair, which consists in applying an α -keto acid solution to the hair for 15 to 120 minutes, then drying and, finally, straightening the head of hair with an iron at a temperature of about 200°C. The α -keto acid employed is preferably glyoxylic acid. However, it has been noted that glyoxylic acid may not be well tolerated, in particular when the scalp is sensitive and/or irritated. Its volatility, amplified by the use of heat from the iron, can also be a problem. Furthermore, the compositions of the prior art may adversely affect the hair and/or adversely affect its colour. Treatments using a composition comprising a base combined with a heat treatment have also been proposed for straightening the hair. Such treatments make it possible to obtain good relaxing of curls, but can lead to modifications of the hair fibre. Document EP 1837010 especially describes a straightening/relaxing process using a composition comprising sodium hydroxide and a heat treatment. Document WO 2007/144707 describes a straightening/relaxing process using a composition comprising a non-hydroxylated base such as monoethanolamine or ethylenediamine, combined with a heat treatment. Document WO 2009/117344 also describes a straightening/relaxing process using a composition comprising a non-hydroxylated base and a protein-denaturing agent, combined with a heat treatment. In order to limit hair fibre modifications, it has also been proposed to use compositions comprising weak acids at alkaline pH, combined with a heat treatment. Document WO 2010/049434 describes, for example, a straightening/relaxing process in which a composition comprising a dicarboxylic acid, such as maleic acid, and heat treatment are applied.

Moreover, compounds of bithiolactone type are known in the adhesives and coating field (FR30204734). The bithiolactones described comprise two thiolactone groups separated by an alkylene or amide group. These compounds have not been used in the cosmetics field.

There is still a need to develop a process for treating keratin materials, in particular keratin fibres such as the hair, more particularly a process for shaping or straightening/relaxing keratin fibres in a way that is efficient and long-lasting, while

limiting degradation of the hair, in particular persistent with respect to successive shampooing operations.

This (these) objective(s) is (are) achieved through the use of a composition comprising at least one symmetric or asymmetric, preferably symmetric, bisthiolactone, chosen from the compounds of formula **(I)** below:



and also the organic or mineral acid or base salts thereof, the optical isomers thereof, and the solvates thereof such as hydrates;

in which formula **(I)**:

- 10 • **X** and **X'**, which may be identical or different, represent an oxygen or sulfur atom, preferably an oxygen atom;
- **Y** and **Y'**, which may be identical or different, represent an oxygen or sulfur atom or a group NR with R representing a hydrogen atom or a (C₁-C₆)alkyl group, preferably Y and Y' represent an oxygen atom;
- 15 • **R₁**, **R₂**, **R₃** and **R₄**, which may be identical or different, represent a hydrogen atom or an optionally substituted (C₁-C₆)alkyl group, such as methyl, ethyl or hydroxyethyl, preferably R₁, R₂, R₃ and R₄ are identical, particularly R₁, R₂, R₃ and R₄ represent a hydrogen atom;
- **a**, **b**, **c** and **d**, which may be identical or different, preferably are identical, 20 represent an integer inclusively between 0 and 4, with the sum of a + b inclusively between 2 and 5, in particular between 2 and 3, more particularly 2, and the sum of c + d inclusively between 2 and 5, in particular between 2 and 3, more particularly 2, preferentially a=b=c=d, more preferentially a=b=c=d=1;
- **A** and **A'**, which may be identical or different, preferably are identical, 25 represent an oxygen atom or an amino group -N(R₅)- with R₅ representing a hydrogen atom or an optionally substituted (C₁-C₆)alkyl group, such as methyl or hydroxyethyl; preferably, R₅ represents a hydrogen atom;
- **B** represents a linear or branched, saturated or unsaturated, preferably saturated, 30 divalent hydrocarbon-based chain comprising from 2 to 18 carbon atoms, which is in particular C₄-C₁₆, linear or branched, optionally substituted, optionally cyclic

and/or interrupted with one or more non-contiguous groups or atoms chosen from
i) oxygen atoms, ii) sulfur atoms, iii) $-N(R_6)-$, iv) $-N^+(R_6)(R_7)-$, Q^- with R_6 and R_7 ,
which may be identical or different, being as defined for R_5 , preferably R_6 and R_7
represent a hydrogen atom or a (hydroxy)(C_1 - C_4)alkyl group such as methyl, ethyl
5 or hydroxyethyl and Q^- representing an anionic counterion, such as halide (Cl^- or
 Br^-).

Another subject of the invention is a process for treating keratin materials, in
particular keratin fibres, in particular human keratin fibres such as the hair, for shaping
10 keratin fibres and/or straightening/relaxing said materials, using the compound(s) of
formula (I) as defined previously.

Another subject of the invention is the compounds of formula (I) as defined
previously.

15 Another subject of the invention is a process for preparing the compounds of
formula (I) as defined previously.

Another subject of the invention is the cosmetic use of the compounds of formula
20 (I) as defined previously, in particular for treating keratin fibres, in particular human
keratin fibres such as the hair, preferably for shaping keratin fibres and/or
straightening/relaxing said fibres.

The compounds of formula (I) of the invention, as defined previously, make it
25 possible in particular to obtain good relaxing of curls, that is long-lasting in particular
with respect to shampooing operations, while at the same time limiting degradation of
the hair.

The compounds of formula (I) as defined previously have in particular the
advantage of conferring good persistence, after shampooing, of good cosmetic
30 properties of conditioning said materials. Thus, the keratin materials treated are
conditioned in a long-lasting manner.

Other characteristics and advantages of the invention will emerge more clearly on
reading the description and the examples that follow.

In the following text, unless indicated otherwise:

- 35
- the term "*organic or mineral acid salt*" is intended to mean cosmetically acceptable organic or mineral acid salts, more particularly the salts chosen from a salt derived from i) hydrochloric acid HCl , ii) hydrobromic acid HBr , iii) sulfuric acid H_2SO_4 , iv) alkylsulfonic acids: $Alk-S(O)_2OH$ such as methanesulfonic acid

and ethanesulfonic acid; v) arylsulfonic acids: $\text{Ar-S(O)}_2\text{OH}$ such as benzenesulfonic acid and toluenesulfonic acid; vi) citric acid; vii) succinic acid; viii) tartaric acid; ix) lactic acid; x) alkoxysulfonic acids: Alk-O-S(O)OH such as methoxysulfonic acid and ethoxysulfonic acid; xi) aryloxysulfonic acids such as tolueneoxysulfonic acid and phenoxysulfonic acid; xii) phosphoric acid H_3PO_4 ; xiii) acetic acid $\text{CH}_3\text{C(O)OH}$; xiv) triflic acid $\text{CF}_3\text{SO}_3\text{H}$; and xv) tetrafluoroboric acid HBF_4 ;

- 10 ▪ The term “*anionic counterion*” is intended to mean an anion or an anionic group derived from an organic or mineral acid salt which counterbalances the cationic charge of the dye; more particularly, the anionic counterion is chosen from: i) halides such as chloride or bromide; ii) nitrates; iii) sulfonates, including $\text{C}_1\text{-C}_6$ alkylsulfonates: $\text{Alk-S(O)}_2\text{O}^-$ such as methylsulfonate or mesylate and ethylsulfonate; iv) arylsulfonates: $\text{Ar-S(O)}_2\text{O}^-$ such as benzenesulfonate and toluenesulfonate or tosylate; v) citrate; vi) succinate; vii) tartrate; viii) lactate; ix) alkyl sulfates: Alk-O-S(O)O^- such as methyl sulfate and ethyl sulfate; x) aryl sulfates: Ar-O-S(O)O^- such as benzene sulfate and toluene sulfate; xi) alkoxy sulfates: $\text{Alk-O-S(O)}_2\text{O}^-$ such as methoxy sulfate and ethoxy sulfate; xii) aryloxy sulfates: $\text{Ar-O-S(O)}_2\text{O}^-$; xiii) phosphates $\text{O=P(OH)}_2\text{O}^-$, $\text{O=P(O}^-\text{)}_2\text{-OH}$, $\text{O=P(O}^-\text{)}_3$, $\text{HO-[P(O)(O}^-\text{)]}_w\text{-P(O)(O}^-\text{)}_2$ with w being an integer; xiv) acetate; xv) triflate; and xvi) borates such as tetrafluoroborate, xvii) disulfate $(\text{O=})_2\text{S(O}^-\text{)}_2$ or SO_4^{2-} and monosulfate HSO_4^- ; oxalate, (bi)carbonate, lactate, formate and propionate; the anionic counterion, derived from an organic or inorganic acid salt, ensures the electrical neutrality of the molecule; thus, it is understood that when the anion comprises several anionic charges, then the same anion may serve for the electrical neutrality of several cationic groups in the same molecule or else may serve for the electrical neutrality of several molecules; for example, a compound of formula (I) which contains two cationic ammonium groups may contain either two “*singly charged*” anionic counterions or a “*doubly charged*” anionic counterion such as $(\text{O=})_2\text{S(O}^-\text{)}_2$ or $\text{O=P(O}^-\text{)}_2\text{-OH}$;
- 30 ▪ the term “*alkyl*” is intended to mean a linear or branched radical containing from 1 to 8 carbon atoms, in particular from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, for example methyl, ethyl, *n*-propyl, isopropyl, butyl, *n*-pentyl, *n*-hexyl, preferably methyl;
- 35 ▪ the term “*alkoxy*” is intended to mean an alkyl oxy group with “*alkyl*” as defined previously;
- 40 ▪ the term “*optionally substituted*” preceding alkyl, hydrocarbon-based chain or alkylene groups is intended to mean that said groups can be substituted with one or more groups, which may be identical or different, chosen from i) hydroxyl, ii) halogen, iii) $(\text{C}_1\text{-C}_4)\text{alkoxy}$, iv) hydroxy $(\text{C}_2\text{-C}_4)\text{alkoxy}$; v) (di)(hydroxy $(\text{C}_1\text{-C}_4)$ (alkyl)amino, vi) $\text{R}_a\text{-Z}_a\text{-C(Z}_b\text{)-Z}_c^-$, and v) $\text{R}_a\text{-Z}_a\text{-S(O)}_t\text{-Z}_c^-$ with

Z_a and Z_b , which may be identical or different, representing an oxygen or sulfur atom or a group NR_a' , Z_c representing a bond, an oxygen or sulfur atom or a group NR_a ; R_a representing a hydrogen atom or a (C₁-C₄)alkyl group and R_a' representing a hydrogen atom or an alkyl group and t is 1 or 2;

- 5 ▪ an "aryl" radical represents a monocyclic or fused or non-fused polycyclic carbon-based group, comprising from 6 to 22 carbon atoms, at least one ring of which is aromatic; in particular, the aryl radical is a phenyl, biphenyl, naphthyl, indenyl, anthracenyl or tetrahydronaphthyl, preferably phenyl;
- 10 ▪ a "heteroaryl radical" represents a 5- to 22-membered, monocyclic or polycyclic, fused or non-fused group, comprising from 1 to 6 heteroatoms chosen from nitrogen, oxygen and sulfur atoms, at least one ring of which is aromatic; preferentially, a heteroaryl radical is chosen from acridinyl, benzimidazolyl, benzobistriazolyl, benzopyrazolyl, benzopyridazinyl, benzoquinolyl, benzothiazolyl, benzotriazolyl, benzoxazolyl, pyridinyl, tetrazolyl, 15 dihydrothiazolyl, imidazopyridinyl, imidazolyl, indolyl, isoquinolyl, naphthoimidazolyl, naphthoxazolyl, naphthopyrazolyl, oxadiazolyl, oxazolyl, oxazolopyridyl, phenazinyl, phenoxazolyl, pyrazinyl, pyrazolyl, pyrilyl, pyrazoyltriazyl, pyridyl, pyridinoimidazolyl, pyrrolyl, quinolyl, tetrazolyl, thiadiazolyl, thiazolyl, thiazolopyridinyl, thiazoylimidazolyl, thiopyrylyl, triazolyl;
- 20 ▪ moreover, the addition salts that may be used in the context of the invention are especially chosen from salts of addition with a cosmetically acceptable base such as the basifying agents as defined below, for instance alkali metal hydroxides, such as sodium hydroxide or potassium hydroxide, aqueous ammonia, amines or alkanolamines;
- 25 ▪ the term "*heterocycloalkyl*" is intended to mean a monocyclic or bicyclic, preferably monocyclic, fused or non-fused group which is saturated or contains one or more ethylenic unsaturations, which is non-aromatic, comprising from 5 to 10 ring members, comprising in at least one ring a heteroatom N, possibly containing from 1 to 3 additional non-adjacent heteroatoms chosen from a 30 nitrogen, oxygen and sulfur atom, this heterocycle possibly being substituted with one or more radicals, which may be identical or different, chosen from alkyl, hydroxyalkyl and alkoxy radicals, preferentially, according to the present invention, the heterocycle is a saturated or unsaturated, preferably saturated, 5- to 8-membered heterocycle, and more preferentially is chosen from piperidyl, 35 pyrrolidinyl, piperazinyl and morpholinyl;
- the term "*cycloalkyl*" is intended to mean a monocyclic or bicyclic, preferably monocyclic, fused or non-fused hydrocarbon-based group which is saturated or contains one or more ethylenic unsaturations, which is non-aromatic,

- comprising from 5 to 10 ring members, this cycloalkyl possibly being substituted with one or more radicals, which may be identical or different, chosen from alkyl, hydroxyalkyl and alkoxy radicals, preferentially, according to the present invention, the cycloalkyl is saturated and comprises from 5 to 8 ring members, and more preferentially is chosen from cyclopentyl and cyclohexyl;
- the term "*cycloalkylene*" is intended to mean a cycloalkyl group as defined previously, which is divalent;
 - the term "*heterocycloalkylene*" is intended to mean a heterocycloalkyl group as defined previously, which is divalent;
 - the term "*cyclic*" is intended to mean that the hydrocarbon-based chain can represent or comprise one or more monocyclic or polycyclic divalent groups comprising from 5 to 18 ring members, which can optionally be interrupted with one or more heteroatoms chosen from oxygen, nitrogen or sulfur; in particular "*cyclic*" represents a cycloalkylene or heterocycloalkylene, preferably cycloalkylene, group as defined previously and more preferentially is chosen from cyclopentylene and cyclohexylene,
 - the "*aryl*" or "*heteroaryl*" radicals or the aryl or heteroaryl part of a radical may be substituted with at least one substituent borne by a carbon atom, chosen from:
 - an optionally substituted C₁-C₆ alkyl radical;
 - a halogen atom;
 - a hydroxyl group;
 - a C₁-C₂ alkoxy radical;
 - a C₂-C₄ (poly)hydroxyalkoxy radical;
 - an amino radical;
 - a 5- or 6-membered heterocycloalkyl radical;
 - a 5- or 6-membered heteroaryl radical, optionally substituted with a (C₁-C₄)alkyl radical, preferentially methyl;
 - an amino radical substituted with one or two identical or different C₁-C₆ alkyl radicals, optionally bearing at least:
 - i) a hydroxyl group,
 - ii) one amino group optionally substituted with one or two optionally substituted C₁-C₃ alkyl radicals, said alkyl radicals possibly forming with the nitrogen atom to which they are attached a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom,

- an acylamino radical ($-\text{NR}-\text{C}(\text{O})-\text{R}'$) in which the R radical is a hydrogen atom or a $\text{C}_1\text{-C}_4$ alkyl radical optionally bearing at least one hydroxyl group and the R' radical is a $\text{C}_1\text{-C}_2$ alkyl radical;
 - a carbamoyl radical ($((\text{R})_2\text{N}-\text{C}(\text{O})-)$ in which the R radicals, which may be identical or different, represent a hydrogen atom or a $\text{C}_1\text{-C}_4$ alkyl radical optionally bearing at least one hydroxyl group;
 - an alkylsulfonylamino radical ($(\text{R}'-\text{S}(\text{O})_2-\text{N}(\text{R})-)$ in which the radical R represents a hydrogen atom or a $\text{C}_1\text{-C}_4$ alkyl radical optionally bearing at least one hydroxyl group and the radical R' represents a $\text{C}_1\text{-C}_4$ alkyl radical or a phenyl radical; an aminosulfonyl radical ($((\text{R})_2\text{N}-\text{S}(\text{O})_2-)$ in which the radicals R, which may be identical or different, represent a hydrogen atom or a $\text{C}_1\text{-C}_4$ alkyl radical optionally bearing at least one hydroxyl group;
 - a carboxylic radical in acid or salified (preferably with an alkali metal or a substituted or unsubstituted ammonium) form;
 - a cyano group;
 - a nitro or nitroso group;
 - a polyhaloalkyl group, preferentially trifluoromethyl;
- the expression "*at least one*" is equivalent to "*one or more*"; and
 - the expression "*inclusively*" for a range of concentrations is intended to mean that the limits of the range are included in the defined range.

The bithiolactone(s)

According to one particular embodiment of the invention, the bithiolactone(s) of formula **(I)** are such that **A** and **A'** represent an identical amino group $-\text{N}(\text{R}_5)-$ with R_5 representing a hydrogen atom or a $(\text{C}_1\text{-C}_4)$ alkyl group, more preferentially A and A' represent a group $-\text{N}(\text{H})-$.

According to another embodiment of the invention, the bithiolactone(s) of formula **(I)** are such that **A** and **A'** represent an oxygen atom.

In particular, the bithiolactone(s) of formula **(I)** of the invention are such that **B** represents a $(\text{C}_2\text{-C}_{16})$ alkylene group optionally interrupted with one or more oxygen atoms, or a group $-\text{N}(\text{R}_6)-$ with R_6 representing a hydrogen atom or a $(\text{C}_1\text{-C}_4)$ alkyl group such as methyl, preferably from 1 to 5 oxygen atoms, such as 2, 3 or 4 non-contiguous oxygen atoms.

More particularly, the bithiolactone(s) of formula **(I)** of the invention are such that **B** represents a divalent group chosen from:

$-(\text{CH}_2-\text{CH}_2-\text{O})_q-(\text{CH}_2)_r-$, $-(\text{CH}_2)_r-(\text{O}-\text{CH}_2-\text{CH}_2)_q-$, $-(\text{CH}_2)_r-(\text{O}-\text{CH}_2-\text{CH}_2)_q-(\text{CH}_2)_t-$,
 $-(\text{CH}_2)_r-(\text{CH}_2-\text{CH}_2-\text{O})_q-(\text{CH}_2)_t-$, $-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O})_q-(\text{CH}_2)_r-$, $-(\text{CH}_2)_r-(\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2)_q-$,
 $-(\text{CH}_2)_r-(\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2)_q-(\text{CH}_2)_t-$ and $-(\text{CH}_2)_r-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O})_q-(\text{CH}_2)_t-$
 with q , r and t , which may be identical or different, representing an integer inclusively
 5 between 0 and 14, and the sum of $q+r$, $q+t$, or $r+q+t$ being inclusively between 4 and 12.

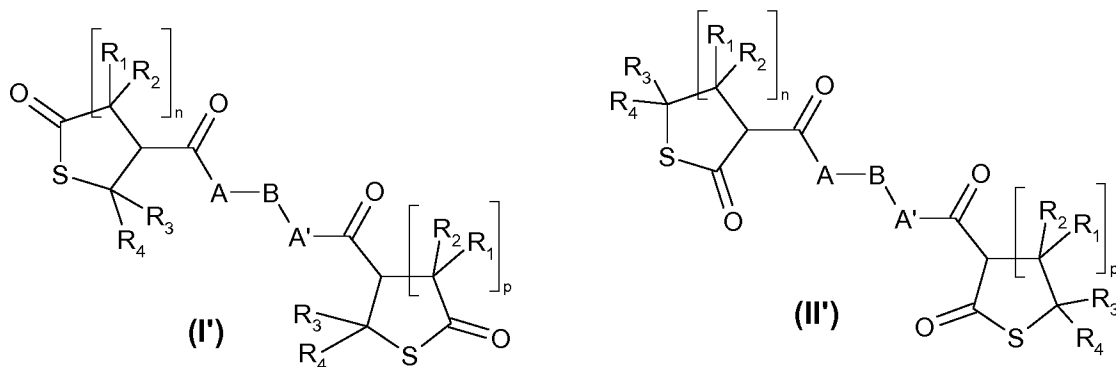
According to another particular embodiment, the bithiolactone(s) of formula **(I)** of the invention are such that **B** represents a divalent group chosen from: $-(\text{CH}_2)_u-\text{N}(\text{R}_6)-(\text{CH}_2)_v-$ and $-(\text{CH}_2)_u-\text{N}^+(\text{R}_6)(\text{R}_7)-(\text{CH}_2)_v-$, Q^- with u and v , which may be identical or
 10 different, representing an integer inclusively between 2 and 14, preferentially between 4 and 8, with Q^- , R_6 and R_7 being as defined previously.

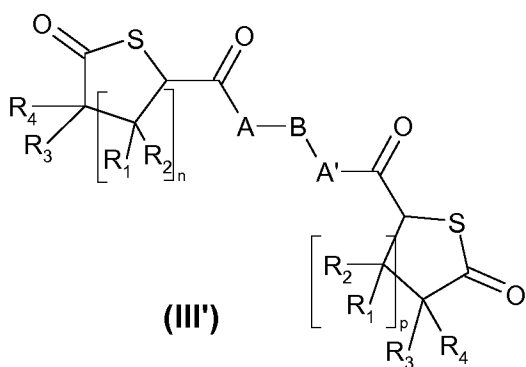
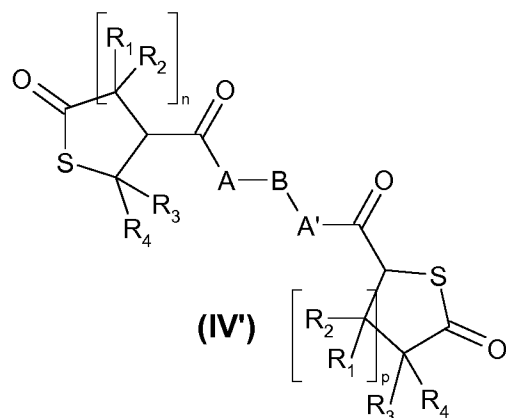
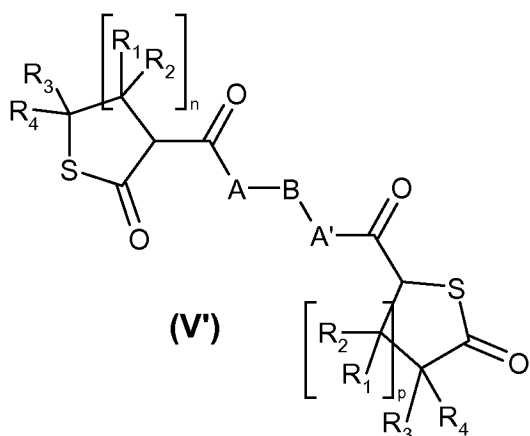
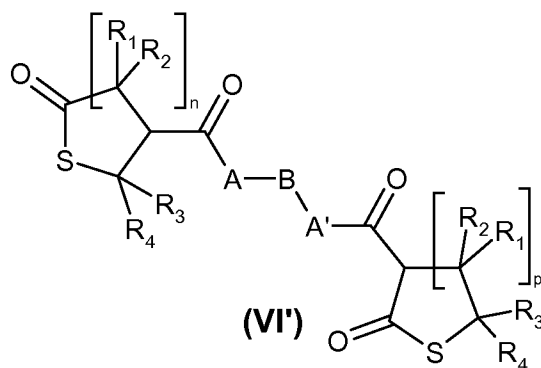
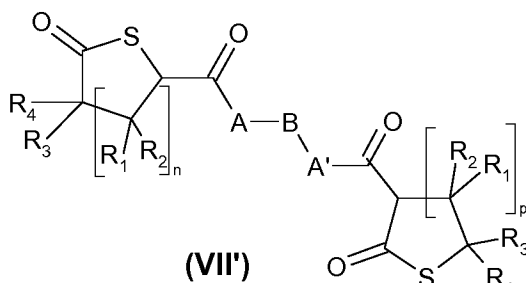
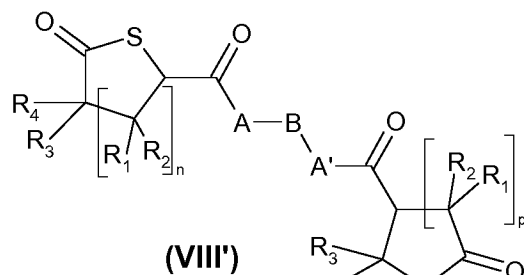
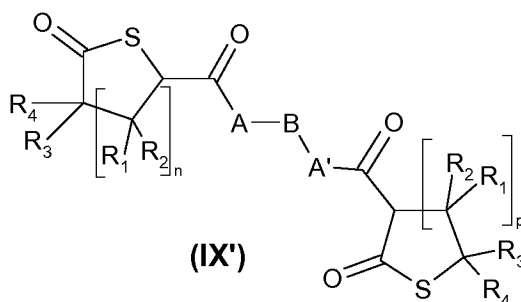
According to another particular embodiment, the bithiolactone(s) of formula **(I)** of the invention are such that **B** represents a divalent group chosen from: and $-(\text{CH}_2)_w-$ with w representing an integer inclusively between 1 and 14, more particularly between
 15 2 and 10, preferentially between 3 and 6, such as 4.

According to another embodiment, **B** represents an optionally substituted monocyclic ($\text{C}_4\text{-C}_7$)cycloalkylene group, such as cyclohexylene.

According to one embodiment, **B** represents a (hetero)arylene group such as phenylene, which is optionally substituted.

20 According to one particular embodiment, the symmetric or asymmetric, preferably symmetric, dithiolactones of the invention are chosen from the compounds of formulae **(I')** to **(IX')** below:





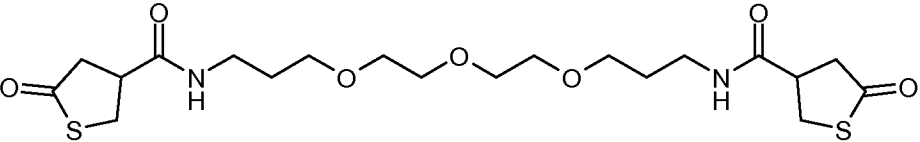
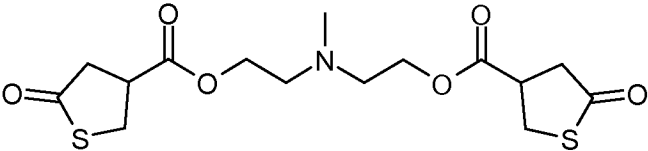
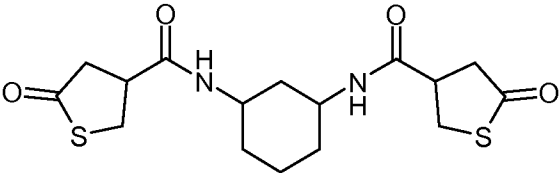
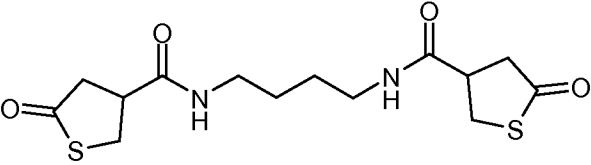
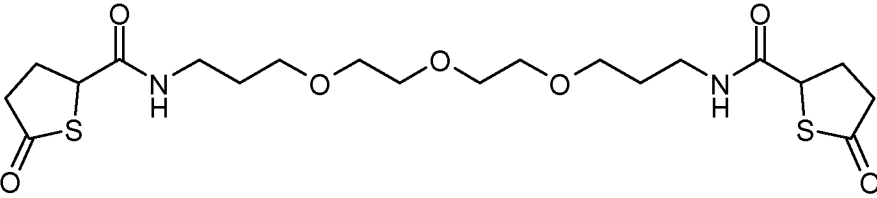
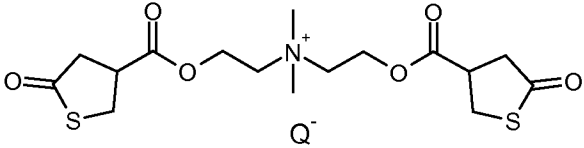
and also the organic or mineral acid or base salts thereof, the optical isomers thereof,
 5 and the solvates thereof such as hydrates;
 in which formulae (I') to (IX'):

- **n** and **p**, which may be identical or different, preferably identical, represent an integer inclusively between 1 and 3, in particular $n = p$ and they are 1 or 2, preferably 1;

- **R₁, R₂, R₃ and R₄**, which may be identical or different, are as defined previously, and preferably represent a hydrogen atom; and
- **A, A' and B** are as defined previously.

According to one advantageous embodiment, the dithiolactone(s) are chosen from the compounds of formulae (I') to (III'), in particular (I') and (III'), preferably (I').

More particularly, the bithiolactones of the invention are chosen from compounds 1 to 6 below:

	<u>1</u>
	<u>2</u>
	<u>3</u>
	<u>4</u>
	<u>5</u>
	<u>6</u>

and also the organic or mineral acid or base salts thereof, the optical isomers thereof, and the solvates thereof such as hydrates, with Q⁻ representing an anionic counterion, in particular halide, such as Cl⁻.

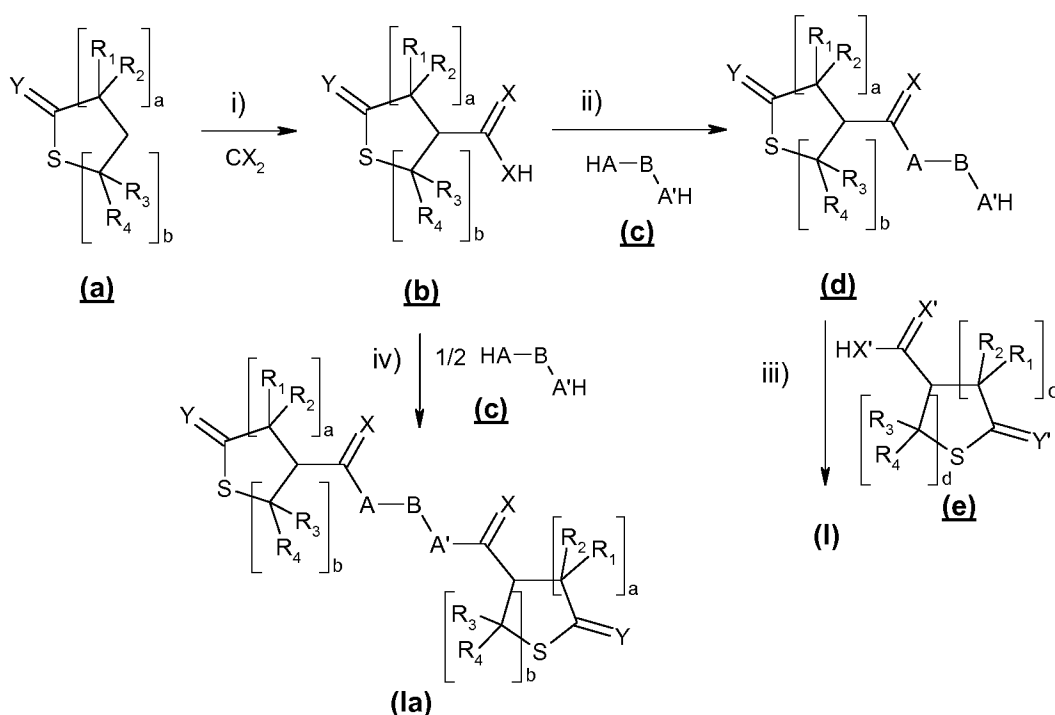
Process for preparing the thiolactone(s)

Another subject of the invention is the process for preparing the bithiolactones of formula **(I)** according to synthesis scheme 1, 2, 3 or 4.

➤ synthesis scheme 1 which consists in reacting:

- in a first step, a thiolactone **(a)** with a strong base, preferably an organolithium base, such as lithium diisopropylamide, then with a reagent CX_2 , in particular CO_2 , preferably at low temperature ($-78^\circ C$), under an inert atmosphere, and in a non-protic solvent such as THF, followed by acidification, preferably with a mineral acid, such as hydrochloric acid, so as to give the thiocarboxylated compound **(b)** (step i));
- in a second step:
 - either one molar equivalent of the compound **(b)** reacts with one equivalent of diol, diamino or alcohol amine **(c)**, preferably in a halogenated solvent such as dichloromethane, at low temperature ($0^\circ C$), so as to give the compound **(d)** (step ii)),
 - or two molar equivalents of the compound **(b)** react with one equivalent of **(c)**, preferably in a halogenated solvent such as dichloromethane, at low temperature ($0^\circ C$), so as to give the compound according to the invention **(Ia)** (step iv));
- in a third step, the compound **(d)** comprising a nucleophilic group $-A'H$ reacts with one molar equivalent of thiocarboxylated thiolactone **(e)**, preferably in a halogenated solvent such as dichloromethane, at low temperature ($0^\circ C$), so as to give the compounds **(I)** according to the invention (step iii); the reagent **(e)** being synthesized under the same conditions as for the reagent **(b)**;

Scheme 1:

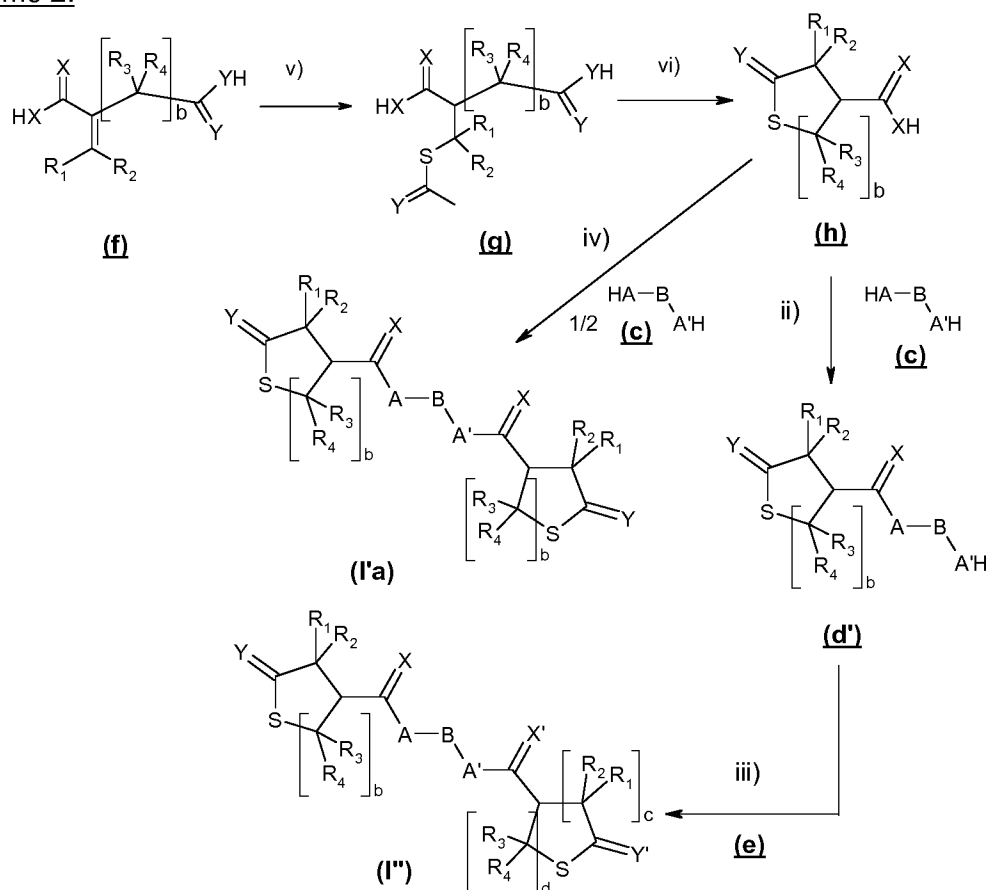


with a, b, c, d, R₁, R₂, R₂, R₄, X, X', Y, Y', A, B, and A' being as defined previously;

➤ synthesis scheme 2 which consists in reacting:

the alpha-ethylenic bis(thio)acid reagent **(f)**, with at least one molar equivalent of a reagent CH₃-C(Y)-SH, preferably in a non-protic solvent such as dichloromethane, or THF, and in particular at a temperature of between 30°C and 100°C, preferably between 40°C and 80°C, so as to give the compound **(g)** (step v); followed by an acidification step, preferably with a mineral acid such as hydrochloric acid (6 N), in particular at a temperature between 50°C and 110°C, preferably between 60°C and 90°C, so as to give the thiolactone **(h)** (step vi)); the latter being able to react according to steps ii), iii) and iv) under the same conditions as scheme 1, so as to give the compound **(l)** or **(la)** according to the invention for which a is 1 corresponding to the compounds of formulae **(l'')** and **(l'a)** respectively:

Scheme 2:



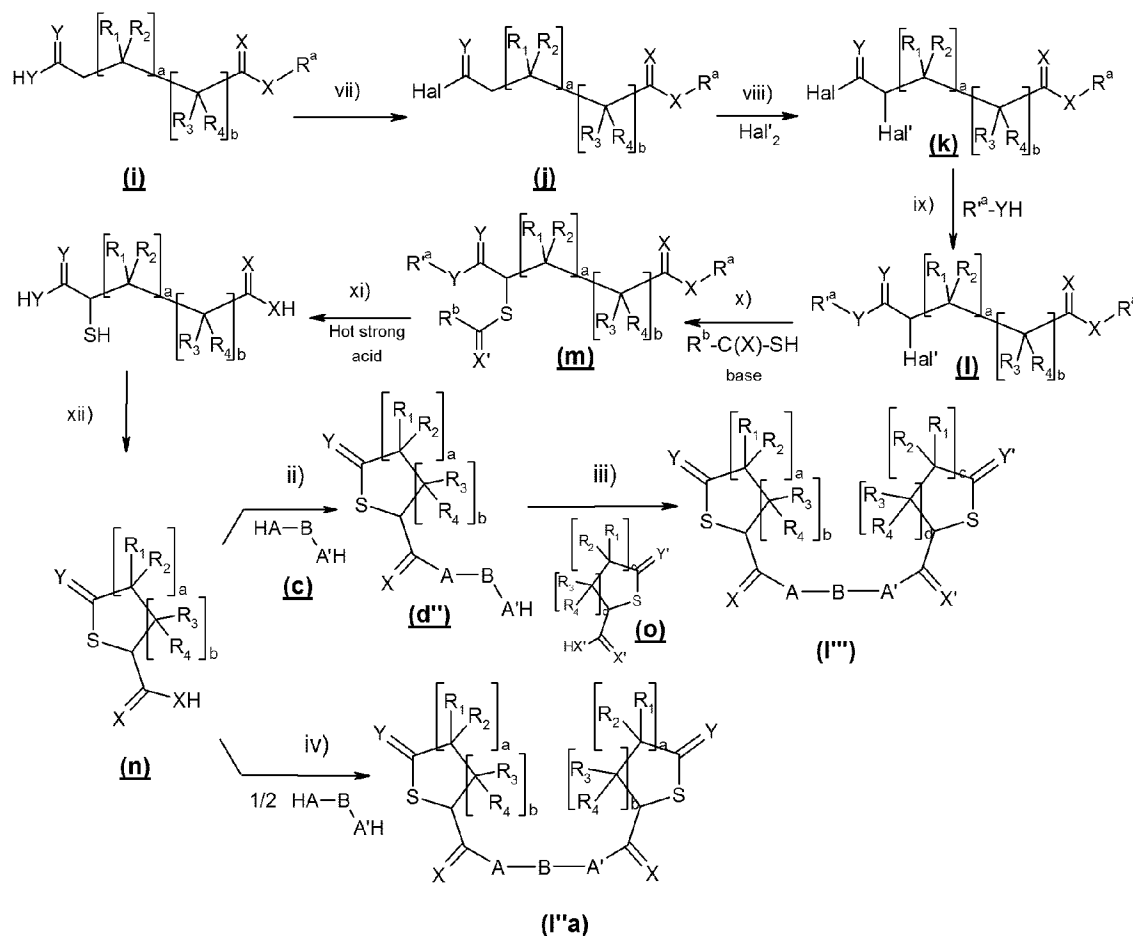
15 with b, R₁, R₂, R₂, R₄, X, X', Y, Y', A, B, and A' being as defined previously;

➤ synthesis scheme 3 which consists in reacting:

the (thio)acid compound **(i)**, with one molar equivalent of a reagent that makes it possible to replace the group -YH of -C(Y)-YH with a halogen atom; preferably, said reagent used is a thionyl or oxalyl halide such as thionyl chloride or oxalyl chloride; in particular, this step is carried out without solvent or with a solvent chosen from

halogenated non-protic solvents such as dichloromethane, so as to give the (thio)acid halide compound **(j)** (step vii); followed by a step of halogenation in the alpha position with respect to the group Hal-C(Y)-, preferably with Br₂ so as to give the dihalogenated compound **(k)** (step viii); preferably, the solvent is evaporated off, and then a thiol or alcohol compound R^a-YH, preferably ethanol, is added, so as to give the bis(thio)ester compound **(l)** (step ix); the latter compound is then reacted with a thiol carboxylic (thio)acid R^b-C(X')-SH, preferably thioacetic acid, in the presence of a base such as sodium ethoxide, in particular in a non-protic solvent such as tetrahydrofuran, so as to give the compound **(m)** (step x); this compound **(m)** is then reacted with an acid, preferably a strong mineral acid such as hydrochloric acid, or an organic acid such as trifluoroacetic acid; in particular, this reaction is carried out under hot conditions, preferably at a temperature between 50°C and 100°C, so as to give the thiolactone **(n)** (step xi); the latter being able to react according to step ii), in the presence of the reagent (o) in place of (e) according to steps iii) and iv) of scheme 1, so as to give the compound **(l)** or **(la)** according to the invention for which a is 1 corresponding to the compounds of formulae **(I''')** and **(I''a)** respectively;

Scheme 3:



with a, b, c, d, R₁, R₂, R₂, R₄, X, X', Y, Y', A, B, and A' being as defined previously, R^a, R^a and R^b, which may be identical or different, representing a (C₁-C₆)alkyl group such as methyl, Hal and Hal', which may be identical or different, represent a halogen atom such as chlorine or bromine, preferably chlorine;

5 ➤ synthesis scheme 4 which consists in reacting:

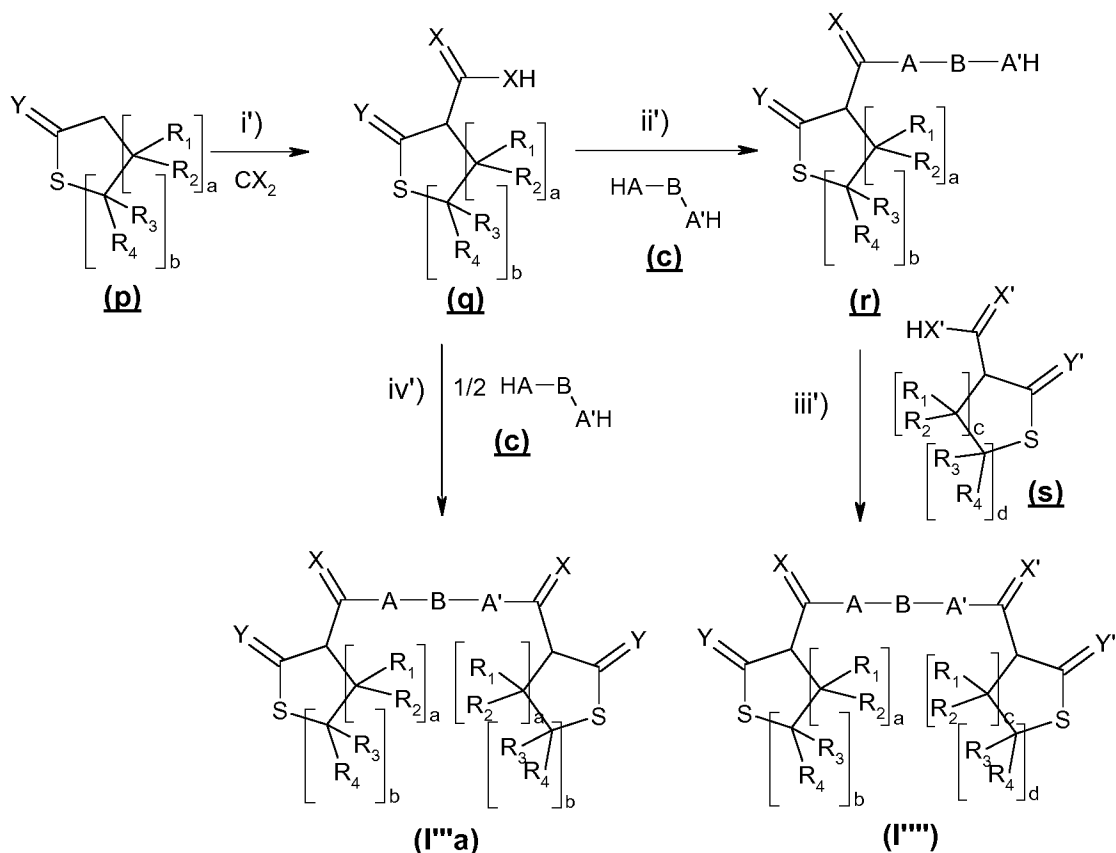
- in a first step, a thiolactone (**p**) with a strong base, preferably an organolithium base, such as lithium diisopropylamide, then with a reagent CX₂, in particular CO₂, preferably at low temperature (-78°C), under an inert atmosphere, and in a non-protic solvent such as THF, followed by acidification, preferably with a mineral acid, such as hydrochloric acid, so as to give the thiocarboxylated compound (**q**) (step i'));

- in a second step:

• either one molar equivalent of the compound (**q**) reacts with one equivalent of diol, diamino or alcohol amine (**r**), preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compound (**s**) (step ii')),

• or two molar equivalents of the compound (**q**) react with one equivalent of (**c**), preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compound according to the invention (**I'''a**) (step iv'));

- in a third step, the compound (**d**) comprising a nucleophilic group -A'H reacts with one molar equivalent of thiocarboxylated thiolactone (**e**), preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compounds (**I''''**) according to the invention (step iii'); the reagent (**e**) being synthesized under the same conditions as for the reagent (**b**);



with a, b, c, d, R₁, R₂, R₂, R₄, X, X', Y, Y', A, B, and A' being as defined previously.

The composition of the invention:

5

The composition of the invention comprises one or more compound(s) of formulae (I) or (I') to (IX') or 1 to 5 as defined previously.

According to one particular embodiment, the composition comprises one or more compound(s) of formulae (I) or (I') to (IX') or 1 to 6 as defined previously, in an amount
10 inclusively between 0.01% and 50% by weight relative to the total weight of the composition, in particular between 0.1% and 30%, more particularly between 1% and 20%, preferentially between 2% and 15%, more preferentially between 5% and 10% by weight relative to the total weight of the composition.

The pH of the composition used in the process of the invention is greater than or
15 equal to 1 or less than or equal to 7. Preferably, the pH of the composition ranges from 2 to 6 and more preferably from 3 to 5.

The compositions

The composition(s) of the invention are cosmetic, that is to say they contain a
20 physiologically acceptable medium, that is to say a medium that is compatible with human keratin materials such as the skin (of the body, face, around the eyes or the scalp), the hair, the eyelashes, the eyebrows, bodily hair, the nails or the lips.

The physiologically acceptable medium of the composition(s) used in the process according to the invention is advantageously an aqueous medium. It may be constituted, for example, of water or of a mixture of water and of at least one cosmetically acceptable organic solvent. Examples of organic solvents that may be mentioned include C₂-C₄ lower alcohols, such as ethanol and isopropanol; polyols, especially those having from 2 to 6 carbon atoms, for instance glycerol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, dipropylene glycol or diethylene glycol; polyol ethers, for instance 2-butoxyethanol, propylene glycol monomethyl ether and diethylene glycol monomethyl ether or monoethyl ether; and mixtures thereof.

The cosmetic compositions of the invention are preferably aqueous and then comprise water at a concentration ranging from 10% to 99.5%, better still from 30% to 95% and even better still from 50% to 90% by weight relative to the total weight of the composition.

The composition used according to the invention may also contain one or more cosmetic additives chosen from non-ionic, anionic, cationic and amphoteric surfactants, vitamins and provitamins, including panthenol, sunscreens, fillers, colorants, nacreous agents, opacifiers, sequestrants, film-forming polymers, cationic, anionic or neutral polymers, associative polymers, plasticizers, silicones, thickeners, oils, antioxidants, antifoams, moisturizers, emollients, penetrants, fragrances and preservatives; preferably one or more non-ionic, anionic, cationic and amphoteric surfactants, cationic, anionic and neutral polymers, or associative polymers.

Depending on their nature and the purpose of the composition, the normal cosmetic ingredients can be present in normal amounts which can be easily determined by those skilled in the art and which can be, for each ingredient, between 0.01% and 80% by weight. A person skilled in the art will take care to choose the ingredients participating in the composition, and also their amounts, so that they do not harm the properties of the compositions of the present invention.

The compositions used in the process according to the invention may be in any of the formulation forms conventionally used, and in particular in the form of an aqueous, alcoholic or aqueous-alcoholic, or oily solution or suspension; a solution or a dispersion of the lotion or serum type; an emulsion, in particular of liquid or semi-liquid consistency, of the O/W, W/O or multiple type; a suspension or emulsion of soft consistency of cream (O/W) or (W/O) type; an aqueous or anhydrous gel, or any other cosmetic form.

These compositions may be packaged in pump-action bottles or in aerosol containers, so as to apply the composition in vaporized (lacquer) form or in the form of a mousse. Such packaging forms are indicated, for example, when it is desired to

obtain a spray or a mousse, for treating the hair. In these cases, the composition preferably comprises at least one propellant.

pH of the composition(s):

5

According to one particular embodiment of the invention, the composition comprising the bithiolactone(s) of formulae **(I)**, or **(I')** to **(IX')** or **1** to **6** as defined previously is aqueous and has an acid pH. Preferentially, the pH is adjusted so that the pH is greater than or equal to 1 and less than 7, in particular greater than or equal to 2 and less than 7, more particularly inclusively between 2.5 and 5, preferably between 3 and 4.

10

According to another particular embodiment of the invention, the composition comprising the bithiolactone(s) of formulae **(I)**, or **(I')** to **(IX')** or **1** to **6** as defined previously is aqueous and has a basic pH. Preferentially, the pH is adjusted so that the pH is greater than 7 and less than or equal to 12, more particularly greater than 8 and less than or equal to 11, more preferentially greater than 9 and less than 10.

15

According to yet another particular embodiment of the invention, the composition comprising the bithiolactone(s) of formulae **(I)**, or **(I')** to **(IX')** or **1** to **6** as defined previously is aqueous and has a neutral pH.

20 The pH values may be adjusted by an organic or inorganic acid, or by an alkaline agent chosen from inorganic or organic or hybrid alkaline agents or mixtures thereof.

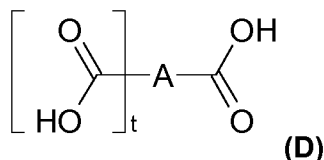
The term "*organic acid*" is intended to mean an acid, i.e. a compound that is capable of releasing a cation or proton H^+ or H_3O^+ , in aqueous medium, which comprises at least one optionally unsaturated, linear or branched C_1 - C_{20} hydrocarbon-based chain, a (hetero)cycloalkyl or (hetero)aryl group and at least one acid chemical function chosen in particular from carboxyl $C(O)OH$, sulfuric SO_3H , SO_2H , and phosphoric PO_3H_2 , PO_4H_2 .

25

More particularly, the acids used are chosen from hydrochloric acid HCl , hydrobromic acid HBr , sulfuric acid H_2SO_4 , alkylsulfonic acids: $(C_1-C_6)Alk-S(O)_2OH$ such as methylsulfonic acid and ethylsulfonic acid; arylsulfonic acids: $Ar-S(O)_2OH$ such as benzenesulfonic acid and toluenesulfonic acid; $(C_1-C_6)alkoxysulfinic$ acids: $Alk-O-S(O)OH$ such as methoxysulfinic acid and ethoxysulfinic acid; aryloxysulfinic acids such as tolueneoxysulfinic acid and phenoxy sulfinic acid; phosphoric acid H_3PO_4 ; triflic acid CF_3SO_3H and tetrafluoroboric acid BF_4 , and carboxylic acid(s) of formula **(D)**

30

35 below:



in which formula **(D)** or a salt thereof:

A represents a saturated or unsaturated, cyclic or non-cyclic and aromatic or non-aromatic hydrocarbon-based group, which is monovalent when *t* is 0 or polyvalent when *t* is greater than or equal to 1, comprising from 1 to 50 carbon atoms, which is optionally interrupted with one or more heteroatoms and/or optionally substituted, especially with one or more hydroxyl groups; preferably, **A** represents a monovalent (C₁-C₆)alkyl group or a polyvalent (C₁-C₆)alkylene group optionally substituted with one or more hydroxyl groups.

Particularly, the carboxylic acids of formula (II) as defined above, and preferably the acid(s) used, is (are) an alpha-hydroxy acid such as lactic acid, glycolic acid, tartaric acid or citric acid.

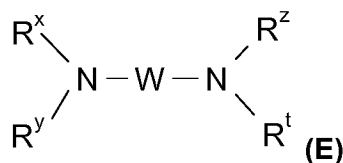
The mineral alkaline agent(s) are preferably chosen from aqueous ammonia, alkali metal carbonates or bicarbonates such as sodium or potassium carbonates and sodium or potassium bicarbonates, sodium hydroxide or potassium hydroxide, or mixtures thereof.

According to one advantageous embodiment of the invention, the alkaline agent(s) are organic amines, i.e. they contain at least one substituted or unsubstituted amino group.

The organic alkaline agent(s) are more preferentially chosen from organic amines with a pK_b at 25°C of less than 12, preferably of less than 10 and more advantageously still of less than 6. It should be noted that it concerns the pK_b corresponding to the function having the highest basicity.

Hybrid compounds that may be mentioned include the salts of the amines mentioned previously with acids such as carbonic acid or hydrochloric acid.

The organic alkaline agent(s) are chosen, for example, from alkanolamines, oxyethylenated and/or oxypropylenated ethylenediamines, amino acids and the compounds of formula **(E)** below:



in which formula **(E)**:

- **W** is a divalent C₁-C₆ alkylene radical optionally substituted with a hydroxyl group or a C₁-C₆ alkyl radical, and/or optionally interrupted with one or more heteroatoms such as oxygen or NR^u;
- **R^x**, **R^y**, **R^z**, **R^t** and **R^u**, which may be identical or different, represent a hydrogen atom or a C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl or C₁-C₆ aminoalkyl radical.

Preferably, the alkanolamine is ethanolamine (or monoethanolamine).

In one variant of the invention, the composition comprises, as alkaline agent, one or more alkanolamines (preferably ethanolamine) and aqueous ammonia. In this variant, the alkanolamine(s) are present in a predominant amount relative to the aqueous ammonia.

According to one particular embodiment of the invention, the composition comprising the bithiolactone(s) of formula (I) as defined previously is aqueous and has an acid pH. Preferentially, the pH is adjusted so that the pH is greater than or equal to 1 and less than 7, in particular greater than or equal to 2 and less than 7, more particularly inclusively between 2.5 and 5, preferably between 3 and 4. In particular, NH₄OH or a citrate buffer can be used.

According to another particular embodiment of the invention, the composition comprising the bithiolactone(s) of formula (I) as defined previously is aqueous and has a basic pH. Preferentially, the pH is adjusted so that the pH is greater than 7 and less than or equal to 12, more particularly greater than 8 and less than or equal to 11, more preferentially greater than 9 and less than 10.

According to yet another particular embodiment of the invention, the composition comprising the bithiolactone(s) of formula (I) as defined previously is aqueous and has a neutral pH.

Process for treating keratin fibres

Thus, one subject of the present invention is a process for treating keratin materials, in particular keratin fibres, in particular human keratin fibres such as the hair, comprising:

- a) the application to said keratin materials of a composition containing at least one bithiolactone chosen from those of formula **(II)** and of formulae **(I')** to **(IX')** and **1** to **6** as defined previously, and also the organic or mineral acid or base salt forms thereof, the optical isomers thereof, and the solvates thereof such as hydrates.

According to one particular embodiment of the invention, the process is a process for treating keratin materials, in particular human keratin fibres such as the hair, comprising:

- 5 a) the application to said keratin materials of a composition containing at least one bisthiolactone chosen from those of formula **(I)** and of formulae **(I')** to **(IX')** and **1** to **6** as defined previously, and also the organic or mineral acid or base salt forms thereof, the optical isomers thereof, and the solvates thereof such as hydrates,
- 10 b) followed by step of straightening/relaxing said keratin materials by means of a straightening iron at a temperature of at least 100°C or a step of shaping the keratin fibres.

The straightening iron is used at a temperature of at least 100°C, preferably at a temperature between, limits included, 100°C and 300°C, preferably between 120°C and 280°C, more preferably between 150°C and 250°C, and even better still between 200 and 250°C.

- 15 The composition of the invention can be applied to dry or wet keratin materials, preferably to dry or damp hair, preferably to dry hair.

The bath ratio of the applied composition may range from 0.1 to 10, more particularly from 0.2 to 5 and preferably between 0.5 and 3. The term "bath ratio" is intended to mean the ratio between the total weight of the applied composition and the total weight of keratin materials to be treated.

20

The process of the invention may comprise other intermediate steps aimed at improving the straightening of the keratin fibres.

In particular, the step of applying the composition may be followed by a leave-on time. The leave-on time, namely the time of contact of the composition on the hair, is preferably at least 5 minutes, preferably between 10 and 60 minutes and preferably between 15 and 45 minutes.

25

Rinsing of the hair can optionally be envisaged after the application of the composition and optionally the leave-on time.

The hair may then optionally be wrung dry, preferably wrung dry.

- 30 A step of drying with a hairdryer, optionally combined with straightening with a brush (blow-drying) may be envisaged before the step of straightening using a straightening iron.

According to one particular embodiment, the straightening with the straightening iron is performed in several passes on the hair, in general 3 to 10 passes.

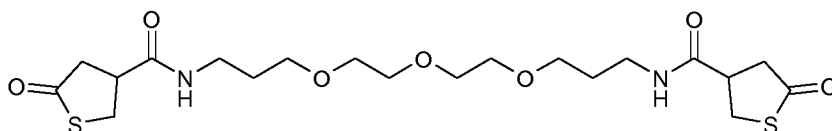
- 35 According to one particular embodiment, the process of the invention comprising the steps of applying the composition according to the invention to the hair, then of straightening with an iron, is carried out one or more times, optionally separated by one

or more cosmetic treatments, preferably shampooing, until the desired shape or shape intensity is obtained.

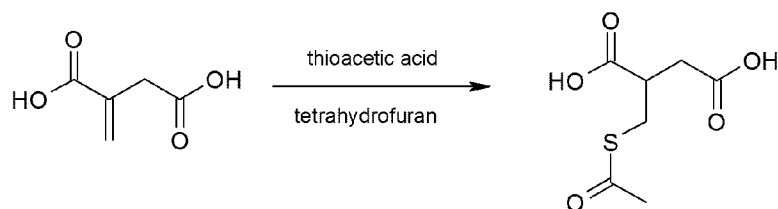
The examples that follow serve to illustrate the invention without, however, being limiting in nature.

EXAMPLES**Example 1:**

Compound 1: Synthesis of 5-oxo-N-[15-oxo-15-(5-oxotetrahydrothiophen-3-yl)-4,7,10-trioxa-14-azapentadec-1-yl]tetrahydrothiophene-3-carboxamide



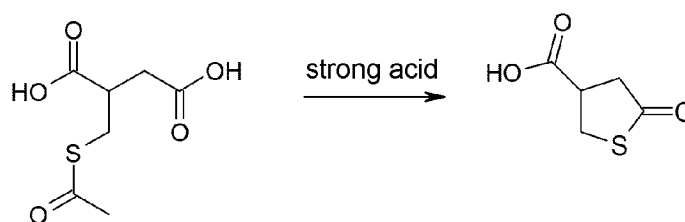
1st step: Synthesis of 2-[(acetylsulfanyl)methyl]butanedioic acid



10 Procedure:

10.0 grams of itaconic acid (0.0769 mol) were placed in 80 ml of tetrahydrofuran (THF) in a 250 ml three-necked flask equipped with a thermometer, a condenser, an argon inlet, a bubbler, a dropping funnel and a magnetic stirrer. A solution containing 5.4 g of thioacetic acid (0.1046 mol) in 100 ml of THF was then added dropwise while keeping the temperature below 5°C. The reaction medium, with stirring, was left to return to ambient temperature and then refluxed for 5 h while monitoring the progress of the reaction by thin layer chromatography. The reaction medium was left at ambient temperature for 8 hours and then concentrated under reduced pressure. The residue, thus obtained, was taken up with heptane in order to crystallize the expected compound. The precipitate obtained was then filtered on sintered glass, and dried under vacuum in the presence of P₂O₅ to constant weight. A white powder was thus obtained, the analyses of which are in accordance with the chemical structure.

2nd step: Synthesis of 5-oxotetrahydrothiophene-3-carboxylic acid



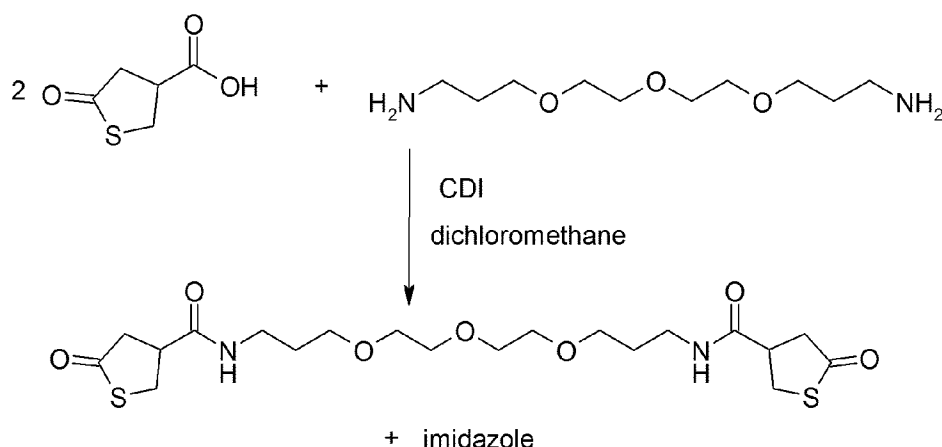
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Procedure:

14.9 g of 2-acetylsulfanylmethyl-5-hydroxy-4-oxopentanoic acid (0.0723 mol) were placed in 45 ml of trifluoroacetic acid (0.5894 mol) in a 250 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. The reaction medium was brought to reflux of the trifluoroacetic acid for 5 hours 30 minutes. The solvent was evaporated off under reduced pressure in order to eliminate all of the trifluoroacetic acid, then the reaction medium was taken up in 100 ml of diisopropyl ether with stirring. The precipitate obtained was recovered by filtration and then washed with 50 ml of diisopropyl ether. A beige powder was thus obtained after drying, the analyses of which are in accordance with the chemical structure.

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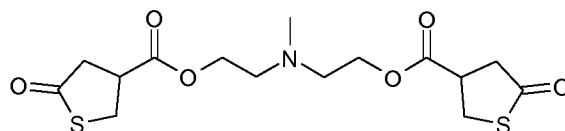
3rd step: Synthesis of 5-oxo-N-[15-oxo-15-(5-oxotetrahydrothiophen-3-yl)-4,7,10-trioxa-14-azapentadec-1-yl]tetrahydrothiophene-3-carboxamide

15 *Procedure:*

15.9 g of 5-oxotetrahydrothiophene-3-carboxylic acid (0.1088 mol) were placed in 300 ml of dichloromethane cooled to 0°C, in a 250 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. 19.5 g of carbonyldiimidazole (CDI) (0.1203 mol) were then added, in small amounts, using a spatula, over the course of 20 minutes. The reaction medium was kept stirring for 30 minutes and then a solution of 12 g of 4,7,10-trioxa-1,13-tridecanediamine (0.0545 mol) dissolved in 60 ml of dichloromethane was added dropwise. The reaction medium was then brought to ambient temperature for 3 hours. 100 ml of a solution of ammonium chloride at 0.25 M were added to the reaction medium. The organic phase was recovered and then washed with three times 100 ml of water. The organic phase was dried over sodium sulfate and was subsequently filtered, then the solvent was evaporated off under reduced pressure. The product was purified by silica column chromatography with 95/5 dichloromethane/methanol as eluent. A grey-white solid was thus obtained after drying, the analyses of which are in accordance with the chemical structure.

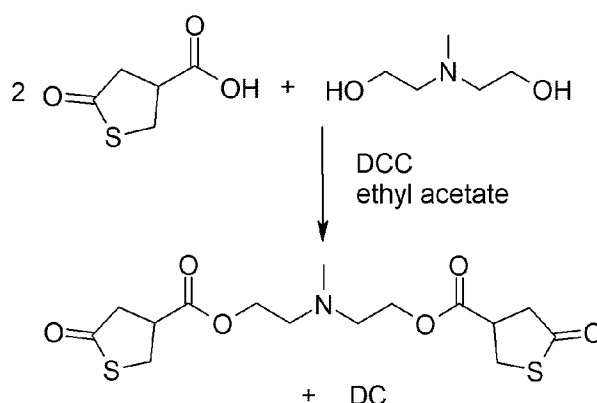
Example 2:

Compound 2: Synthesis of (methylimino)diethane-2,1-diylbis(5-oxotetrahydrothiophene-3-carboxylate)



1st and 2nd step identical to compound 1

3rd step: Synthesis of (methylimino)diethane-2,1-diylbis(5-oxotetrahydrothiophene-3-carboxylate)



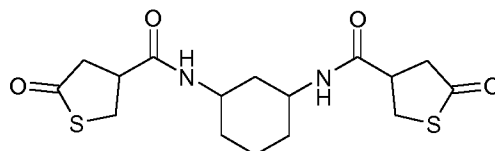
2.9 g of 5-oxotetrahydrothiophene-3-carboxylic acid (0.0336 mol) were placed in 100 ml of ethyl acetate in a 250 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. 2.0 g of N-methyldiethanolamine (0.0168 mol) were then added. The reaction medium was cooled to 0°C in an ice bath and then 7.6 g of dicyclohexylcarbodiimide (DCC) (0.0369 mol) were added in small amounts over the course of 10 minutes. The reaction medium was then brought to ambient temperature for 1 hour 30 minutes. The DCU formed was eliminated by filtration on sintered glass and the filtrate was evaporated under reduced pressure. The residue obtained was purified by silica column chromatography with 95/5 dichloromethane/ethanol as eluent. A light yellow oil was thus obtained after drying, the analyses of which are in accordance with the chemical structure.

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Example 3:

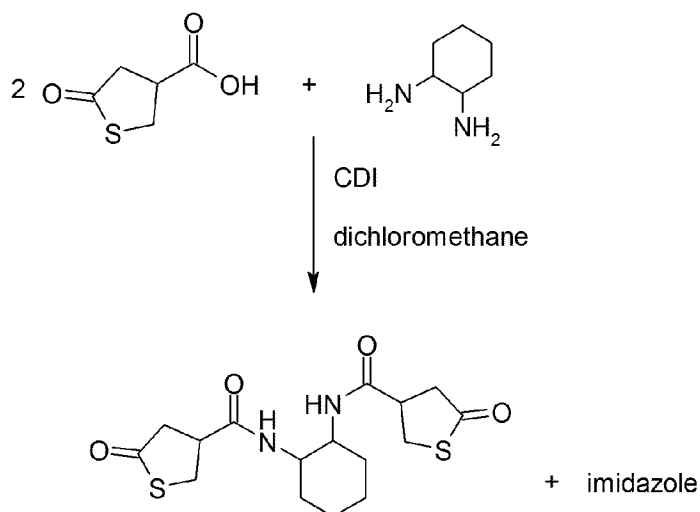
Compound 3: Synthesis of N,N'-cyclohexane-1,3-diylbis(5-oxotetrahydrothiophene-3-carboxamide)

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1st and 2nd step identical to compound 1

5 3rd step: *Synthesis of N,N'-cyclohexane-1,3-diylbis(5-oxotetrahydrothiophene-3-carboxamide)*



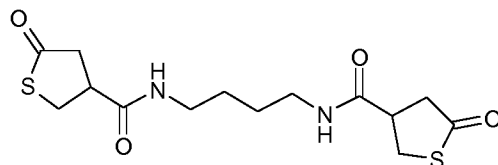
Procedure:

10 10 g of 5-oxotetrahydrothiophene-3-carboxylic acid (0.0684 mol) were placed in 100 ml of dichloromethane cooled to 0°C, in a 250 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. 12.1 g of CDI (0.0746 mol) were then added, in small amounts, using a spatula, over the course of 20 minutes. The reaction medium was kept stirring for 30 minutes and then a solution of 3.9 g of 1,2-cyclohexylamine (0.0341 mol) dissolved in 50 ml of dichloromethane was added dropwise. The reaction medium was then brought to ambient temperature for 3 hours and then left at ambient temperature overnight. 200 ml of water were then added, and the resulting mixture was filtered on sintered glass. The precipitate was washed with water and then with acetone.

20 The ketone phase, containing the desired product, was recovered and then evaporated under reduced pressure. The precipitate was then dried under vacuum to constant weight. A white powder was thus obtained after drying, the analyses of which are in accordance with the chemical structure (4 diastereoisomers identified).

Example 4:

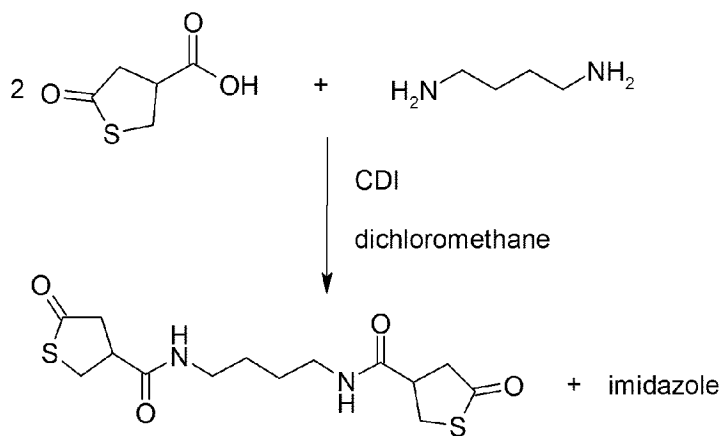
Compound 4: Synthesis of N,N'-butane-1,4-diylbis(5-oxotetrahydrothiophene-3-carboxamide)



1st and 2nd step identical to compound 1

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3rd step: Synthesis of N,N'-butane-1,4-diylbis(5-oxotetrahydrothiophene-3-carboxamide)

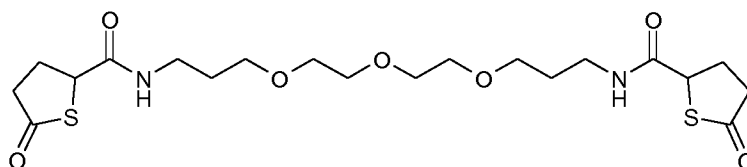


Procedure:

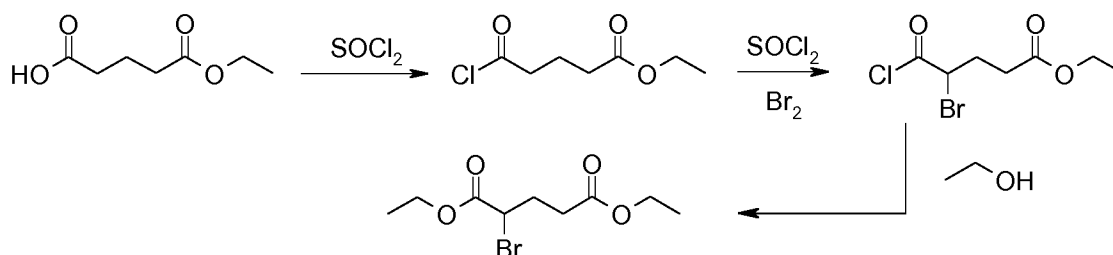
- 10 5 g of 5-oxotetrahydrothiophene-3-carboxylic acid (0.068 mol) were placed in 40 ml of dichloromethane cooled to 0°C, in a 250 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. 6.1 g of N,N-carbonyldiimidazole (0.074 mol) were then added, in small amounts, using a spatula, over the course of 20 minutes. The reaction medium was kept stirring for 30 minutes and then a solution of
- 15 2.84 g of 1,4-diaminobutane (0.034 mol) dissolved in 50 ml of dichloromethane was added dropwise. The reaction medium was then brought to ambient temperature for 3 hours and then left at ambient temperature overnight. It was then filtered on sintered glass and then the precipitate was washed with heptane.
- The precipitate was then dried under vacuum to constant weight. A white powder was
- 20 thus obtained after drying, the analyses of which are in accordance with the chemical structure.

Compound 5: 5-Oxo-N-[15-oxo-15-(5-oxotetrahydrothiophen-2-yl)-4,7,10-trioxa-14-azapentadec-1-yl]tetrahydrothiophene-2-carboxamide

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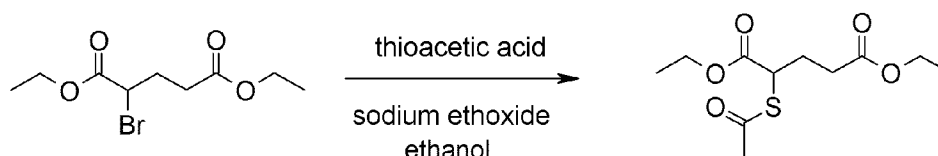
1st step: Synthesis of diethyl 2-bromopentanedioate:



Procedure:

- 5 80 g of 5-ethoxy-5-oxopentanoic acid (0.5 mol) were placed in 150 ml of thionyl chloride in a 1 l three-necked flask equipped with a thermometer, a condenser, an argon inlet, a bubbler, a dropping funnel and a magnetic stirrer. The mixture was then brought, with stirring, to the reflux of the thionyl chloride for 4 hours and then 80 g of bromine (0.5 mol) were added dropwise so as to maintain the bromine vapours in the reactor. The reflux was thus maintained for 5 hours after the addition of bromine and then the mixture was allowed to return to ambient temperature.
- 10 Evaporation under reduced pressure was then carried out in order to obtain a lightly coloured oil. This oil was then added, dropwise, to 500 ml of ethanol while keeping the temperature at 10°C by means of an ice bath. Evaporation under reduced pressure was subsequently carried out, and then the residue was purified by vacuum distillation.
- 15 A colourless oil was thus obtained, the analyses of which are in accordance with the chemical structure.

2nd step: Synthesis of diethyl 2-(acetylsulfanyl)pentanedioate



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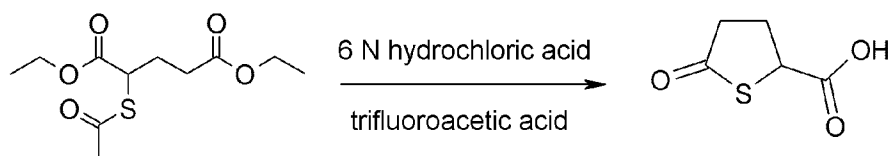
Procedure:

- 78 g (0.292 mol) were placed in 500 ml of ethanol, in a 1 l three-necked flask equipped with a thermometer, a condenser, an argon inlet, a bubbler, a dropping funnel and a magnetic stirrer, and then the mixture was cooled to 0°C by means of an ice bath. 25 ml of thioacetic acid (0.35 mol) were then added, followed by 20 g of sodium ethoxide (0.294 mol) which was added in small portions so as to keep the temperature below 5°C. Stirring was maintained and then the mixture was allowed to return to ambient temperature and the progress of the reaction was monitored by thin layer
- 25

chromatography. The precipitate formed was then filtered off and the filtrate was evaporated under reduced pressure. The oil obtained was then dissolved in 300 ml of dichloromethane and then the organic phase was washed with 200 ml of sodium hydrogen carbonate solution, 2000 ml of 2 N hydrochloric acid and 200 ml of a saturated solution of ammonium chloride.

The organic phase was then dried, followed by evaporation under reduced pressure. A yellow oil was thus obtained, the analyses of which are in accordance with the chemical structure.

10 3rd step: Synthesis of 5-oxotetrahydrothiophene-2-carboxylic acid



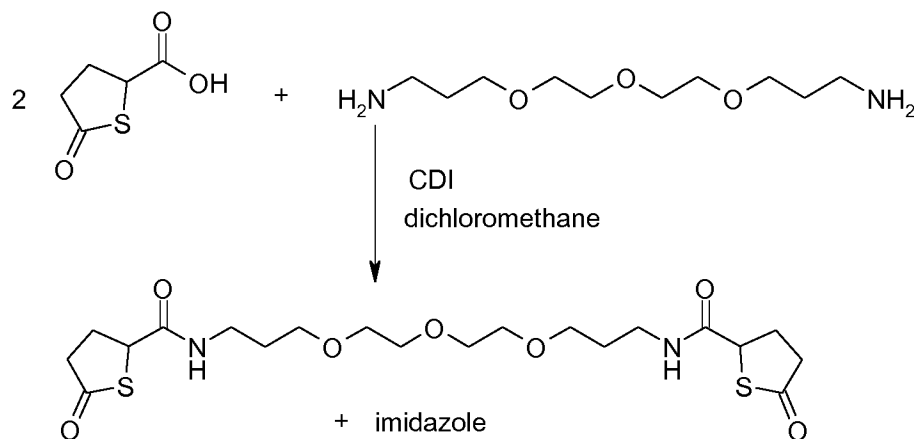
Procedure:

20 g of diethyl 2-(acetylsulfanyl)pentanedioate (0.072 mol) were placed in 200 ml of 6 N hydrochloric acid in a 1 l three-necked flask equipped with a thermometer, a condenser, an argon inlet, a bubbler and a magnetic stirrer. The mixture was then brought to reflux, with stirring, for 6 hours and then evaporated under reduced pressure so as to obtain a yellow oil. It was then placed in a 500 ml reactor with 200 ml of trifluoroacetic acid and then brought to reflux for 6 hours. The progress of the reaction was thus monitored by thin layer chromatography.

Evaporation under reduced pressure was then carried out and the oil was then taken up with ethyl ether in order to crystallize the compound.

An off-white powder was thus obtained, the analyses of which are in accordance with the chemical structure.

25 4th step: Synthesis of 5-oxo-N-[15-oxo-15-(5-oxotetrahydrothiophen-2-yl)-4,7,10-trioxo-14-azapentadec-1-yl]tetrahydrothiophene-2-carboxamide



Procedure:

8 g of 5-oxotetrahydrothiophene-2-carboxylic acid (0.0544 mol) were placed in 150 ml of dichloromethane cooled to 0°C, in a 250 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. 9.75 grams of carbonyldiimidazole (0.0601 mol) were then added, in small amounts, using a spatula, over the course of 20 minutes. The reaction medium was kept stirring for 30 minutes and then a solution of 6 g of 4,7,10-trioxa-1,13-tridecanediamine (0.02725 mol) dissolved in 30 ml of dichloromethane was added dropwise. The reaction medium was then brought to ambient temperature for 3 hours. 50 ml of a solution of ammonium chloride at 0.25 M were added to the reaction medium. The organic phase was recovered and then washed with three times 50 ml of water. The organic phase was dried over sodium sulfate and was subsequently filtered, then the solvent was evaporated off under reduced pressure. The product was purified by silica column chromatography with 95/5 dichloromethane/methanol as eluent. A grey-white solid was thus obtained after drying, the analyses of which are in accordance with the chemical structure.

Application examples (straightening):

20 *Application protocol:*

Before applying the active agents, the hair is washed according to the following protocol:

Step 1: Application of cleansing shampoo (so as to obtain clean hair):

1. Weigh out 0.4 ml of cleansing shampoo per gram of hair in a watch glass.
2. Wet the lock with tap water, passing the lock between the fingers for 5 seconds.
3. Drain the lock of hair dry between two fingers.
4. Apply the cleansing shampoo along the lock of hair (from the root to the end homogeneously).

5. Massage the lock gently between two fingers along its length (so as to work the shampoo into a lather) for 15 seconds from top to bottom (without making knots).
6. Rinse under tap water for 10 seconds, passing the lock between the fingers.
7. Drain the lock dry between two fingers.
- 5 8 Comb the lock.
9. Dry the lock with a hairdryer.

Protocol for applying the active agents of the invention:

10 Step 2: Application of the test product of the invention:

1. Prepare the solution of the active agent at 5% or 10% w/w in water or an aqueous-alcoholic solution containing no more than 30% alcohol.
2. Place a 2.7 g lock in a channel.
- 15 3. Apply the solution of the test product along the lock of hair (from the root to the end homogeneously).
4. Leave it on for 30 minutes.
5. Drain the lock dry between two fingers.
6. Blow dry 20 times.
- 20 7. Pass the straightening iron over 10 times at 230°C over the course of 30 seconds.

The locks are then shampooed according to the following protocol, which may be repeated according to the number of shampoo washes performed:

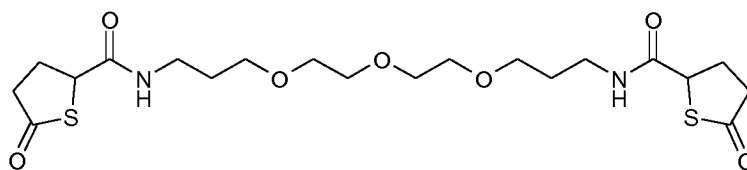
25 Step 3: Application of Shampoo (Persistence):

1. Weigh out 0.4 ml of DOP camomile shampoo per gram of hair in a watch glass.
2. Wet the lock with tap water, passing the lock between the fingers for 5 seconds.
3. Drain the lock of hair dry between two fingers.
- 30 4. Apply the cleansing shampoo along the lock of hair (from the root to the end homogeneously).
5. Massage the lock gently between two fingers along its length (so as to work the shampoo into a lather) for 15 seconds from top to bottom (without making knots).
6. Rinse under tap water for 10 seconds, passing the lock between the fingers.
- 35 7. Drain the lock dry between two fingers.
- 8 Comb the lock.
9. Repeat steps 4 to 8 as many times as there are shampoo washes to be performed (1 to 20 shampoo washes).
10. Dry the lock under a hood.

Result

Example (1) of application with the bistiobutyrolactone compound (5) at 10% by weight in water and 30% by weight of ethanol, pH = 7.

5



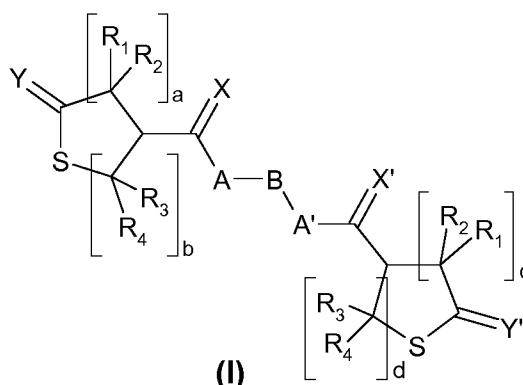
Compound (5)

According to photos 1 and 2, it appears that the straightening effect obtained with the composition of the invention is persistent even after 10 successive shampooing operations.

15

CLAIMS

1. Composition comprising at least one symmetric or asymmetric bithiolactone, chosen from the compounds of formula (I) below:



and also the organic or mineral acid or base salts thereof, the optical isomers thereof, and the solvates thereof such as hydrates;

in which formula (I):

- **X** and **X'**, which may be identical or different, represent an oxygen or sulfur atom, preferably an oxygen atom;
- **Y** and **Y'**, which may be identical or different, represent an oxygen or sulfur atom or a group NR with R representing a hydrogen atom or a (C₁-C₆)alkyl group, preferably Y and Y' represent an oxygen atom;
- **R₁**, **R₂**, **R₃** and **R₄**, which may be identical or different, represent a hydrogen atom or a (C₁-C₆)alkyl group which is optionally substituted, such as methyl, ethyl or hydroxyethyl;
- **a**, **b**, **c** and **d**, which may be identical or different, preferably are identical, represent an integer inclusively between 0 and 4, with the sum of a + b inclusively between 2 and 5, in particular between 2 and 3, more particularly 2, and the sum of c + d inclusively between 2 and 5, in particular between 2 and 3, more particularly 2, preferentially a=b=c=d, more preferentially a=b=c=d=1;
- **A** and **A'**, which may be identical or different, preferably are identical, represent an oxygen atom or an amino group -N(R₅)- with R₅ representing a hydrogen atom or an optionally substituted (C₁-C₆)alkyl group, such as methyl or hydroxyethyl; preferably, R₅ represents a hydrogen atom;

B represents a linear or branched, saturated or unsaturated, preferably saturated, divalent hydrocarbon-based chain comprising from 2 to 18 carbon atoms, which is in particular C₄-C₁₆, linear or branched, optionally substituted, optionally cyclic and/or interrupted with one or more non-contiguous groups or atoms chosen from i) oxygen atoms, ii) sulfur atoms, iii) -N(R₆)-, iv) -N⁺(R₆)(R₇)-, Q⁻ with R₆ and R₇, which may be

identical or different, being as defined for R_5 , preferably R_6 and R_7 represent a hydrogen atom or a (hydroxy)(C_1 - C_4)alkyl group such as methyl, ethyl or hydroxyethyl and Q^- representing an anionic counterion, such as halide (Cl^- or Br^-).

5 **2.** Composition according to the preceding claim, in which the bithiolactone(s) of formula **(I)** are symmetric.

3. Composition according to either one of the preceding claims, in which the bithiolactone(s) of formula **(I)** are such that **A** and **A'** represent an identical amino
10 group $-N(R_5)-$ with R_5 representing a hydrogen atom or a (C_1 - C_4)alkyl group, particularly **A** and **A'** represent a group $-N(H)-$.

4. Composition according to either one of Claims 1 and 2, in which the bithiolactone(s) of formula **(I)** are such that **A** and **A'** represent an oxygen atom.
15

5. Composition according to any one of the preceding claims, in which the bithiolactone(s) of formula **(I)** are such that **B** represents a (C_2 - C_{16})alkylene group optionally interrupted with one or more oxygen atoms, or a group $-N(R_6)-$ with R_6 representing a hydrogen atom or a (C_1 - C_4)alkyl group such as methyl, preferably from
20 1 to 5 oxygen atoms, such as 2, 3 or 4 non-contiguous oxygen atoms; more particularly the bithiolactone(s) of formula **(I)** of the invention are such that **B** represents a divalent group chosen from:

$-(CH_2-CH_2-O)_q-(CH_2)_r-$, $-(CH_2)_r-(O-CH_2-CH_2)_q-$, $-(CH_2)_r-(O-CH_2-CH_2)_q-(CH_2)_t-$,
 $-(CH_2)_r-(CH_2-CH_2-O)_q-(CH_2)_t-$, $-(CH_2-CH_2-CH_2-O)_q-(CH_2)_r-$, $-(CH_2)_r-(O-CH_2-CH_2-$
25 $CH_2)_q-$, $-(CH_2)_r-(O-CH_2-CH_2-CH_2)_q-(CH_2)_t-$ and $-(CH_2)_r-(CH_2-CH_2-CH_2-O)_q-(CH_2)_t-$
 with q , r and t , which may be identical or different, representing an integer inclusively between 0 and 14, and the sum of $q+r$, $q+t$, or $r+q+t$ being inclusively between 4 and 12.

30 **6.** Composition according to any one of Claims 1 to 4, in which the bithiolactone(s) of formula **(I)** are such that **B** represents a divalent group chosen from: and $-(CH_2)_u-N(R_6)-(CH_2)_v-$ with u and v , which may be identical or different, representing an integer inclusively between 2 and 14, preferentially between 4 and 8, with R_6 representing a hydrogen atom or a (hydroxy)(C_1 - C_4)alkyl group such as methyl,
35 ethyl or hydroxyethyl.

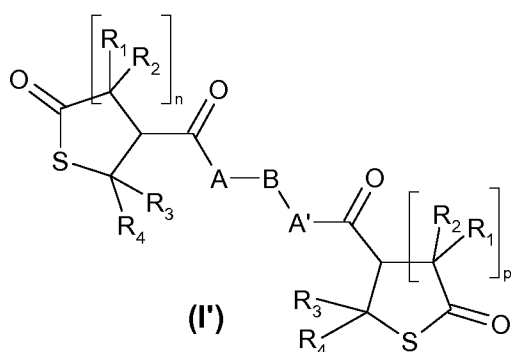
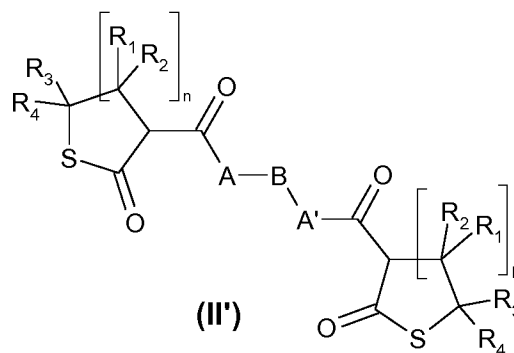
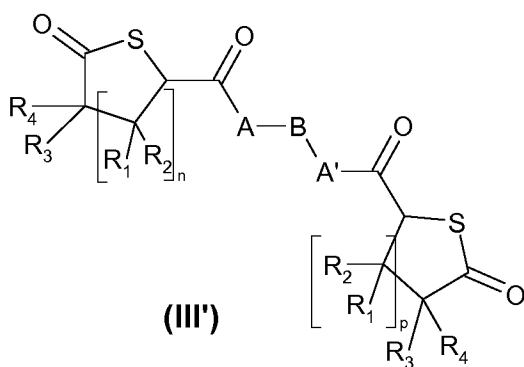
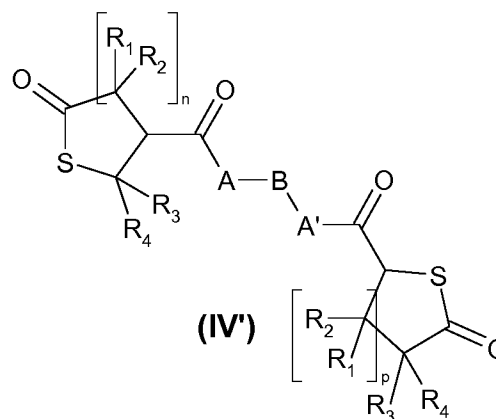
7. Composition according to any one of Claims 1 to 4, in which the bithiolactone(s) of formula **(I)** are such that **B** represents a divalent group chosen

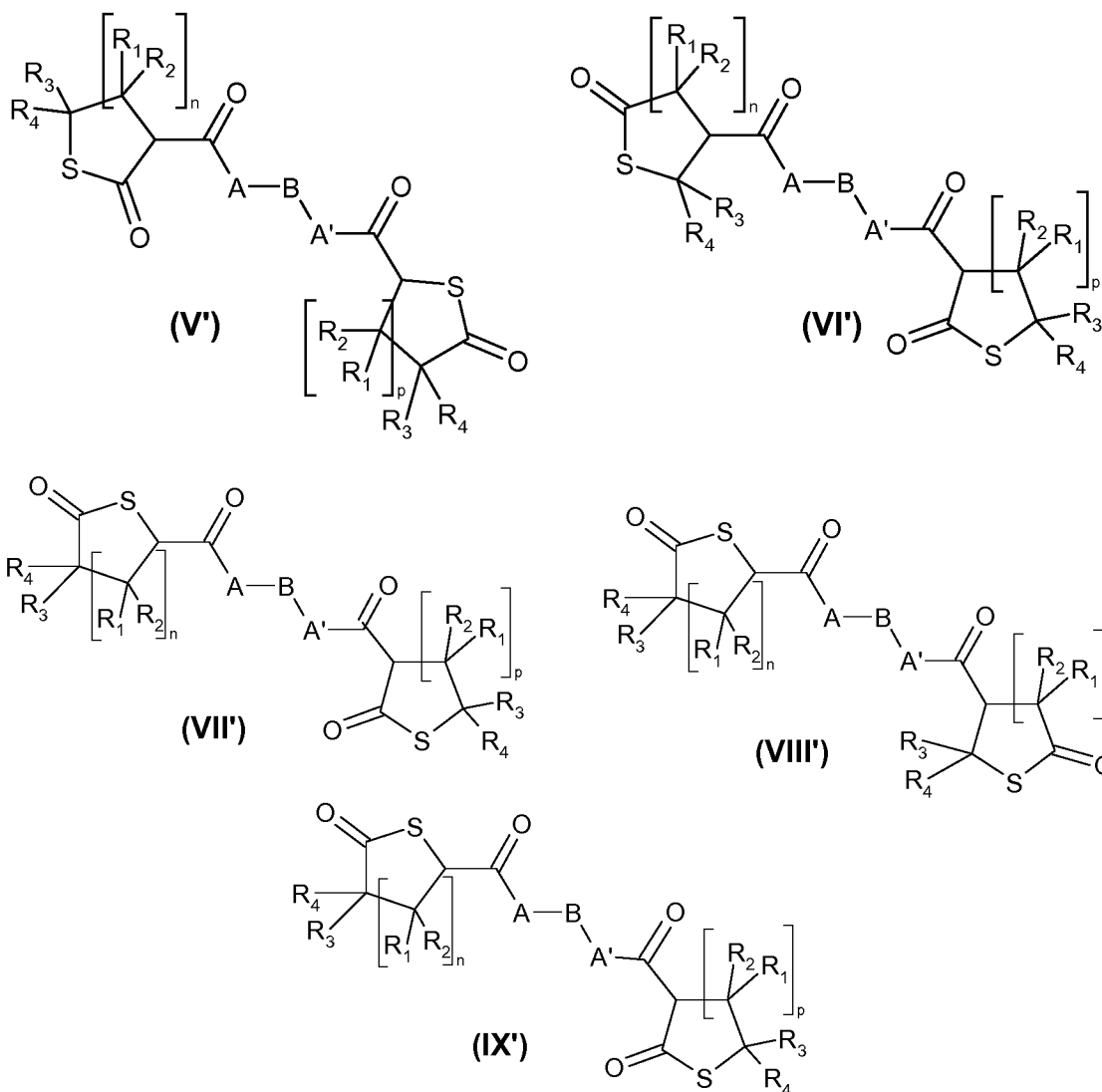
from: and $-(CH_2)_w-$ with w representing an integer inclusively between 1 and 14, more particularly between 2 and 10, preferentially between 3 and 6, such as 4.

8. Composition according to any one of Claims 1 to 4, in which the
5 bithiolactone(s) of formula (I) are such that **B** represents a monocyclic (C_4 - C_7)cycloalkylene group which is optionally substituted, such as cyclohexylene.

9. Composition according to any one of the preceding claims, in which the
10 bithiolactone(s) of formula (I) are such that **R**₁, **R**₂, **R**₃ and **R**₄ are identical, and particularly **R**₁, **R**₂, **R**₃ and **R**₄ represent a hydrogen atom.

10. Composition according to any one of the preceding claims, in which the bithiolactone(s) of formula (I) are chosen from the compounds of formulae (I') to (IX') below:





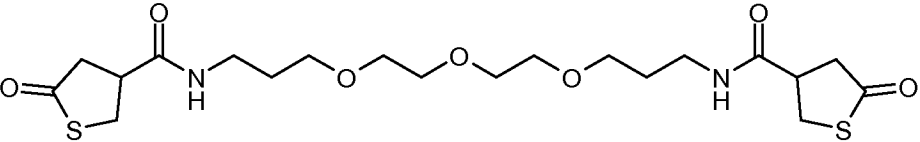
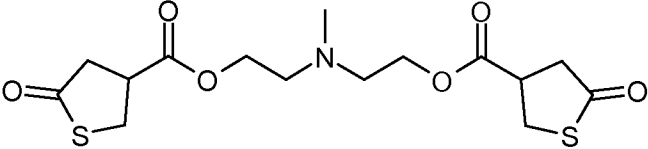
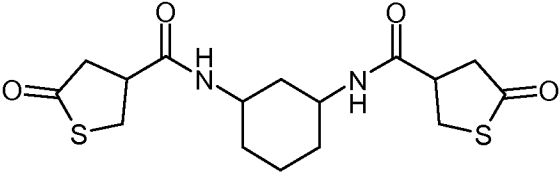
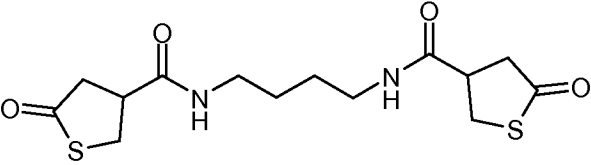
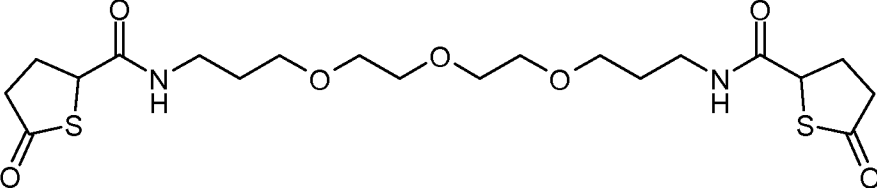
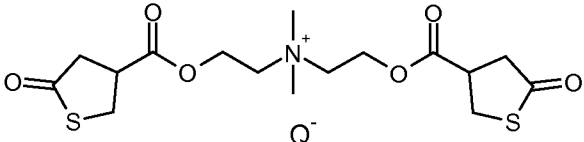
and also the organic or mineral acid or base salts thereof, the optical isomers thereof, and the solvates thereof such as hydrates;

5 in which formulae (I') to (IX'):

- **n** and **p**, which may be identical or different, preferably identical, represent an integer inclusively between 1 and 3, in particular $n = p$ and they are 1 or 2, preferably 1;
- **R₁**, **R₂**, **R₃** and **R₄**, which may be identical or different, are as defined in Claim 1
- 10 or 9; and
- **A**, **A'** and **B** are as defined in any one of Claims 1 and 3 to 8;

particularly, the dithiolactone(s) are chosen from the compounds of formulae (I') to (III'), in particular (I') and (III'), preferably (I').

15 11. Composition according to any one of the preceding claims, in which the bithiolactone(s) of formula (II) are chosen from the compounds of formulae 1 to 5 below

	<u>1</u>
	<u>2</u>
	<u>3</u>
	<u>4</u>
	<u>5</u>
	<u>6</u>

and also the organic or mineral acid or base salts thereof, the optical isomers thereof, and the solvates thereof such as hydrates, with Q⁻ representing an anionic counterion, in particular halide, such as Cl⁻.

- 5 **12.** Composition according to any one of the preceding claims, in which the bithiolactone(s) of formulae **(I)** or **(I')** to **(IX')**, or 1 to 6 are in an amount inclusively between 0.01% and 50% by weight relative to the total weight of the composition, in particular between 0.1% and 30%, more particularly between 1% and 20%, preferentially between 2% and 15%, more preferentially between 5% and 10% by weight relative to the total weight of the composition.
- 10

13. Composition according to any one of the preceding claims, in which the bithiolactone(s) of formulae **(I)**, or **(I')** to **(IX')** or 1 to 6 are aqueous and the pH thereof is acid, preferentially the pH is greater than or equal to 1 and less than 7, in particular

greater than or equal to 2 and less than 7, more particularly inclusively between 2.5 and 5, preferably between 3 and 4.

14. Composition according to any one of Claims 1 to 12, in which the bisthiolactone(s) of formulae **(I)**, or **(I')** to **(IX')** or **1** to **6** are aqueous and the pH thereof is basic, preferentially the pH is greater than 7 and less than or equal to 12, more particularly greater than 8 and less than or equal to 11, more preferentially greater than 9 and less than 10.

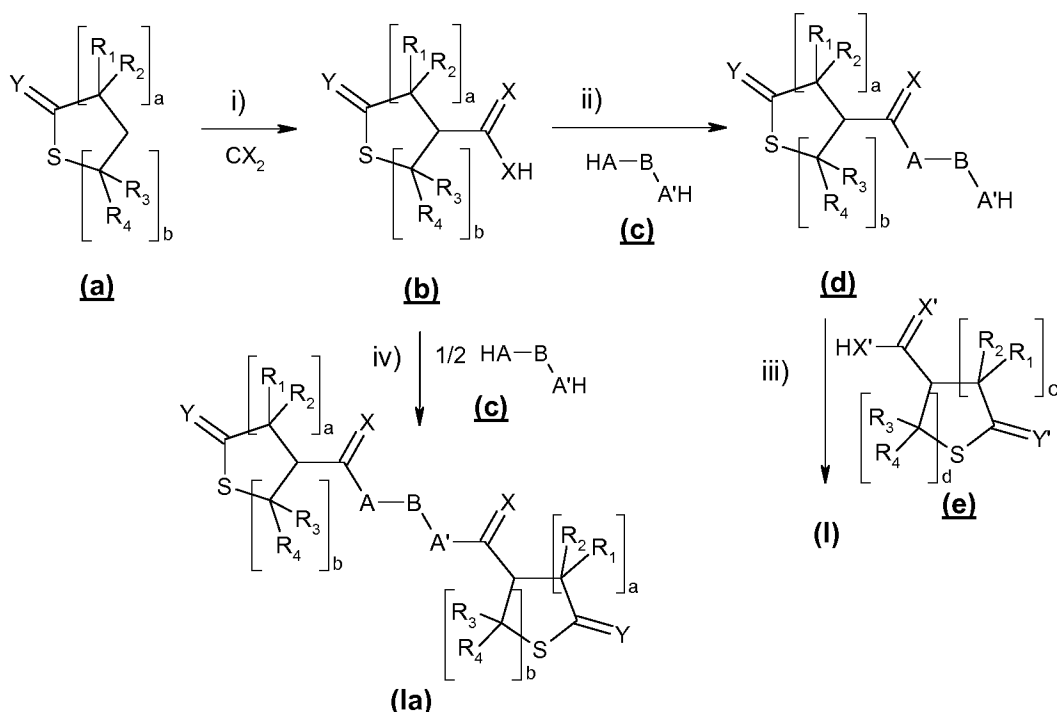
15. Composition according to any one of Claims 1 to 12, in which the bisthiolactone(s) of formulae **(I)**, or **(I')** to **(IX')** or **1** to **6** are aqueous and the pH thereof is neutral.

16. Compound chosen from those of formulae **(I)**, **(I')** to **(IX')**, and **1** to **6** as defined in any one of Claims 1 to 11.

17. Process for preparing the bisthiolactones of formulae **(I)**, **(I')** to **(IX')**, and **1** to **6** as defined in any one of Claims 1 to 11 according to synthesis scheme 1, 2, 3 or 4, ➤ which synthesis scheme 1 consists in reacting:

- in a first step, a thiolactone **(a)** with a strong base, preferably an organolithium base, such as lithium diisopropylamide, then with a reagent CX₂, in particular CO₂, preferably at low temperature (-78°C), under an inert atmosphere, and in a non-protic solvent such as THF, followed by acidification, preferably with a mineral acid, such as hydrochloric acid, so as to give the thiocarboxylated compound **(b)** (step i));
- in a second step:
 - either one molar equivalent of the compound **(b)** reacts with one equivalent of diol, diamino or alcohol amine **(c)**, preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compound **(d)** (step ii)),
 - or two molar equivalents of the compound **(b)** react with one equivalent of **(c)**, preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compound according to the invention **(la)** (step iv));
- in a third step, the compound **(d)** comprising a nucleophilic group –A'H reacts with one molar equivalent of thiocarboxylated thiolactone **(e)**, preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compounds **(I)** according to the invention (step iii); the reagent **(e)** being synthesized under the same conditions as for the reagent **(b)**;

Scheme 1:



with a, b, c, d, R_1 , R_2 , R_3 , R_4 , X, X' , Y, Y' , A, B, and A' being as defined in any one of Claims 1 to 10;

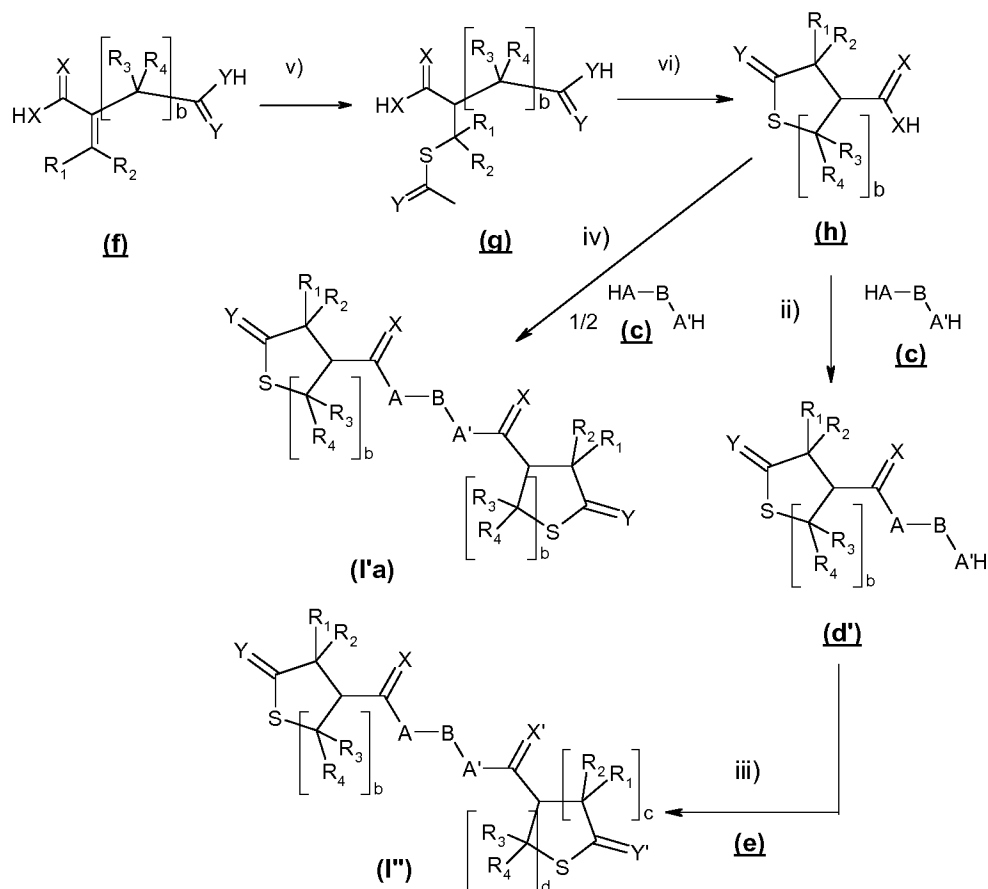
5 ➤ which synthesis scheme 2 consists in reacting:

the alpha-ethylenic bis(thio)acid reagent **(f)**, with at least one molar equivalent of a reagent $CH_3-C(Y)-SH$, preferably in a non-protic solvent such as dichloromethane, or THF, and in particular at a temperature of between $30^\circ C$ and $100^\circ C$, preferably between $40^\circ C$ and $80^\circ C$, so as to give the compound **(g)** (step v); followed by an

10 acidification step, preferably with a mineral acid such as hydrochloric acid (6 N), in particular at a temperature between $50^\circ C$ and $110^\circ C$, preferably between $60^\circ C$ and $90^\circ C$, so as to give the thiolactone **(h)** (step vi)); the latter being able to react according to steps ii), iii) and iv) under the same conditions as scheme 1, so as to give the compound **(I)** or **(Ia)** according to the invention for which a is 1

15 corresponding to the compounds of formulae **(I')** and **(I'a)** respectively:

Scheme 2:



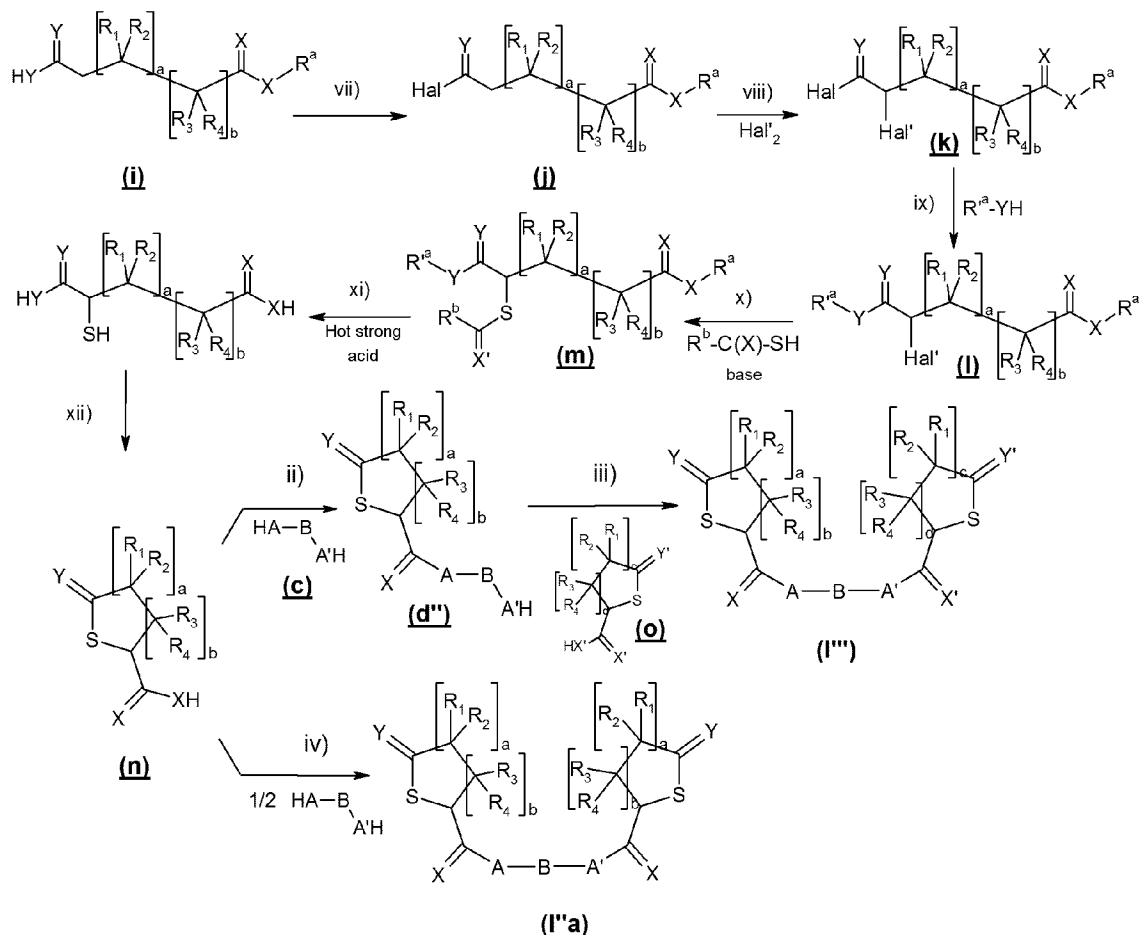
with $b, R_1, R_2, R_3, R_4, X, X', Y, Y', A, B$, and A' being as defined in any one of Claims 1 to 10;

➤ which synthesis scheme 3 consists in reacting:

- 5 the (thio)acid compound **(i)**, with one molar equivalent of a reagent that makes it possible to replace the group $-YH$ of $-C(Y)-YH$ with a halogen atom; preferably, said reagent used is a thionyl or oxalyl halide such as thionyl chloride or oxalyl chloride; in particular, this step is carried out without solvent or with a solvent chosen from halogenated non-protic solvents such as dichloromethane, so as to give the (thio)acid halide compound **(j)** (step vii); followed by a step of halogenation in the
- 10 alpha position with respect to the group $Hal-C(Y)-$, preferably with Br_2 so as to give the dihalogenated compound **(k)** (step viii); preferably, the solvent is evaporated off, and then a thiol or alcohol compound $R^{1a}-YH$, preferably ethanol, is added, so as to give the bis(thio)ester compound **(l)** (step ix); the latter compound is then reacted
- 15 with a thiol carboxylic (thio)acid $R^b-C(X')-SH$, preferably thioacetic acid, in the presence of a base such as sodium ethoxide, in particular in a non-protic solvent such as tetrahydrofuran, so as to give the compound **(m)** (step x); this compound **(m)** is then reacted with an acid, preferably a strong mineral acid such as hydrochloric acid, or an organic acid such as trifluoroacetic acid; in particular, this
- 20 reaction is carried out under hot conditions, preferably at a temperature between $50^\circ C$ and $100^\circ C$, so as to give the thiolactone **(n)** (step xi); the latter being able to

react according to step ii), in the presence of the reagent (o) in place of (e) according to steps iii) and iv) of scheme 1, so as to give the compound **(I)** or **(Ia)** according to the invention for which a is 1 corresponding to the compounds of formulae **(I''')** and **(I''a)** respectively;

5 Scheme 3:

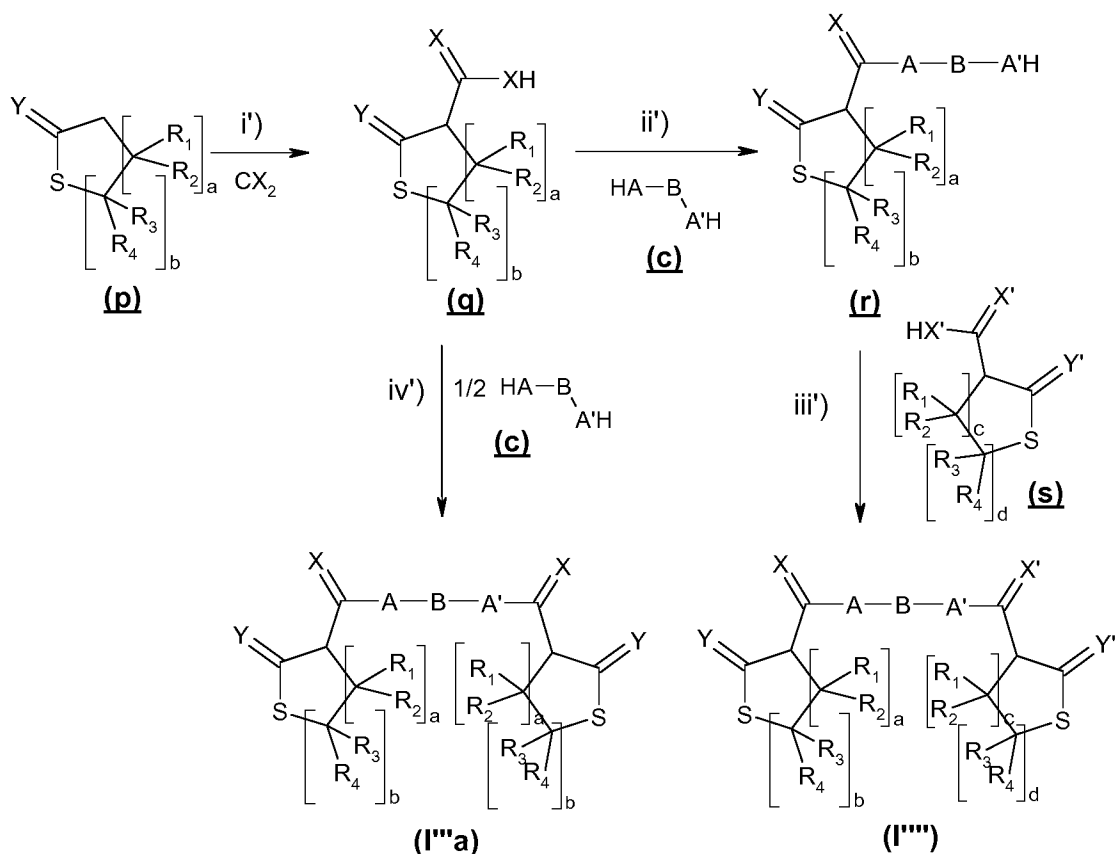


with a, b, c, d, R_1 , R_2 , R_2 , R_4 , X, X' , Y, Y' , A, B, and A' being as defined in any one of Claims 1 to 10, R^a , R'^a and R^b , which may be identical or different, representing a (C_1 - C_6)alkyl group such as methyl, Hal and Hal' , which may be identical or different, represent a halogen atom such as chlorine or bromine, preferably chlorine;

➤ which synthesis scheme 4 consists in reacting:

- in a first step, a thiolactone **(p)** with a strong base, preferably an organolithium base, such as lithium diisopropylamide, then with a reagent CX_2 , in particular CO_2 , preferably at low temperature (-78°C), under an inert atmosphere, and in a non-protic solvent such as THF, followed by acidification, preferably with a mineral acid, such as hydrochloric acid, so as to give the thiocarboxylated compound **(q)** (step i'));
- in a second step:

- either one molar equivalent of the compound **(q)** reacts with one equivalent of diol, diamino or alcohol amine **(r)**, preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compound **(s)** (step ii')),
- 5 • or two molar equivalents of the compound **(q)** react with one equivalent of **(c)**, preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compound according to the invention **(I''a)** (step iv'));
- in a third step, the compound **(d)** comprising a nucleophilic group –A'H reacts
- 10 with one molar equivalent of thiocarboxylated thiolactone **(e)**, preferably in a halogenated solvent such as dichloromethane, at low temperature (0°C), so as to give the compounds **(I''')** according to the invention (step iii'); the reagent **(e)** being synthesized under the same conditions as for the reagent **(b)**;



- 15 with a, b, c, d, R_1 , R_2 , R_2 , R_4 , X, X', Y, Y', A, B, and A' being as defined in any one of Claims 1 to 10.

18. Cosmetic use of one or more bithiolactones chosen from those of
 20 formulae **(I)**, **(I')** to **(IX')**, and **1** to **6** as defined in any one of Claims 1 to 11, in particular for treating keratin fibres, in particular human keratin fibres such as the hair, preferably for shaping keratin fibres and/or straightening/relaxing said fibres.

19. Process for treating keratin materials, in particular human keratin fibres such as the hair, comprising:

- 5 a) the application to said keratin materials of a composition comprising at least one bisthiolactone chosen from those of formulae **(I)**, **(I')** to **(IX')** and **1** to **6** as defined in any one of Claims 1 to 16.

- 20.** Process according to the preceding claim, comprising, after step a), a step b) of straightening/relaxing said keratin materials by means of a straightening iron at a temperature of at least 100°C, or a step of shaping said keratin materials, preferably at a temperature of between, limits included, 100°C and 300°C, preferably between 120°C and 280°C, more preferably between 150°C and 250°C, and even better still between 200 and 250°C.
- 10

Photos 1 and 2

Untreated lock Natural caucasian type IV	Lock treated with example 1 after 10 successive shampoos
	

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/083756

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/49 A61Q5/06 C07D333/32
ADD.

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)

A61K A61Q C07D

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	FR 3 024 734 A1 (XANCHEM [FR]) 12 February 2016 (2016-02-12) cited in the application the whole document	1-20
A	DE 198 26 499 A1 (BEIERSDORF AG [DE]) 16 December 1999 (1999-12-16) the whole document	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ovens, Annabel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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