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(54) **IRIDOID OR SECO-IRIDOID DERIVATIVES AND THEIR USE IN A TANNING PROCESS**

IRIDOID- ODER SECO-IRIDOIDDERIVATE UND IHRE VERWENDUNG IN EINEM GERBVERFAHREN

DÉRIVÉS IRIDOÏDES OU SÉCO-IRIDOÏDES ET LEUR UTILISATION DANS UN PROCÉDÉ DE TANNAGE

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EP 4 379 068 B1

Description

TECHNICAL FIELD

[0001] The present invention relates to the field of tanning. More particularly, the present invention relates to particular iridoid or seco-iridoid derivatives, and their use in a tanning process. It also relates to a process for cross-linking collagen using such derivatives. The invention is set out in the appended set of claims.

TECHNICAL BACKGROUND

[0002] Natural tannins have long been used in processes for tanning skin and stabilizing collagen. Tanning mixtures are mainly composed of polyphenolic tannins, which are divided into two classes: condensed tannins and hydrolysable tannins. The effectiveness of tanning is usually reflected by its ability to stabilize collagen, namely to limit collagen denaturation and impart good resistance to enzymatic hydrolysis. Collagen stabilization can be assessed by measuring the increase in shrinkage temperature, which is correlated to the collagen denaturation temperature. The polyphenolic tannins give rise to a shrinkage temperature around 75-85°C. Other parameters can also be considered for assessing the effectiveness of tanning, such as the mechanical resistance of the hide and its sensory parameters, such as hide filling and suppleness.

[0003] However, due to their astringency, natural polyphenolic tannins lead to a tension of the hide. In order to limit such tension, a pre-tanning step using a metal salt, such as aluminum, iron, zirconium, titanium, or chromium, or synthetic tannins, such as glutaraldehyde or oxazolidine, is required.

[0004] Recently, a new class of natural tanning or pre-tanning agents has been identified: iridoids and seco-iridoids. Among these compounds, genipin can be obtained from geniposide which is extracted from the fruit of *Gardenia jasminoides* or *Genipa americana.* Genipin allows to stabilize the collagen and to reach shrinkage temperatures of 80°C (Zhang et al., JALCA, 2011, 106, 121). Genipin has also been used in combination with an aluminum-based tanning (Ding et al., JALCA, 2008, 103, 377), which resulted in a soft and full leather having a shrinkage temperature of 92°C. Genipin has also been used to cross-link gelatin (Taylor et al., JALCA, 2009, 104, 79). Genipin is readily available in large quantities due to its use as a food coloring agent.

[0005] Other natural iridoids have been used in processes for tanning or pre-tanning hides. In particular, WO2009/065915 describes a tanning method using aglycone derivatives of iridoids and seco-iridoids, different from genipin. Such derivatives can be extracted from olive leaves and are hydrolyzed to give aglycone forms of oleuropein. The mixture obtained by extraction of the leaves in the presence of endogenous enzyme or by the use of acid is not purified and also comprises polyphenolic compounds and compounds derived from hydrolyzed oleuropein, such as (4E)-4-formyl-3-(-1-formyl-2-methoxy-2-oxoethyl)hex-4-enoic acid.

[0006] However, such methods use the aglycone form of iridoids or seco-iridoids, which are highly reactive. This high reactivity can cause several limitations, in particular with regard to the stability, storability, and toxicity. Protected forms of such iridoids or seco-iridoids, in particular glycoside forms, are usually more stable and less toxic, however they are not active in tanning and cannot be easily activated under mild conditions compatible with tanning. In particular, glycosides can only be activated by means of enzymatic hydrolysis, which is expensive, not always reproducible, and not convenient for large-scale processes.

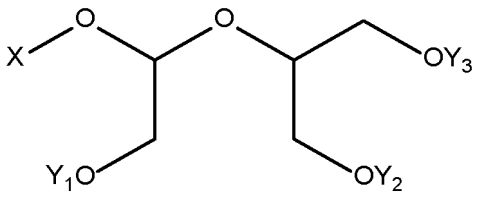
[0007] Document US 2017/080040-A1 discloses a decoction of olive leaves which can be used in the treatment of tanning hides and which comprises an aqueous composition containing at least from about 500 mg/L to about 3,000 mg/L of oleuropein, from about 100 mg/L to about 300 mg/L of hydroxytyrosol, from about 90 mg/L to about 280 mg/L of tyrosol, from about 400 mg/L to about 1,800 mg/L of elenolic acid.

[0008] Therefore, there remains a need to provide efficient pre-tanning or tanning agents that are more stable, have a lower toxicity, and can be activated under mild conditions which can be easily used in tanning processes.

SUMMARY OF THE INVENTION

[0009] In this respect, the inventors have demonstrated that the above limitations could be overcome by protecting the dihydropyranyloxy moiety of iridoid or seco-iridoid compounds with a particular acyclic acetal group. These protected iridoid or seco-iridoid derivatives can advantageously be obtained starting from the corresponding glycoside forms, by successively subjecting the latter to an oxidation and a reduction. This acetal protecting group can be easily removed before and/or during a tanning process, typically using acidic conditions, thereby releasing the active aglycone form.

[0010] Hence, the present invention relates to the use of a compound of formula (I), in a tanning process:



(I),

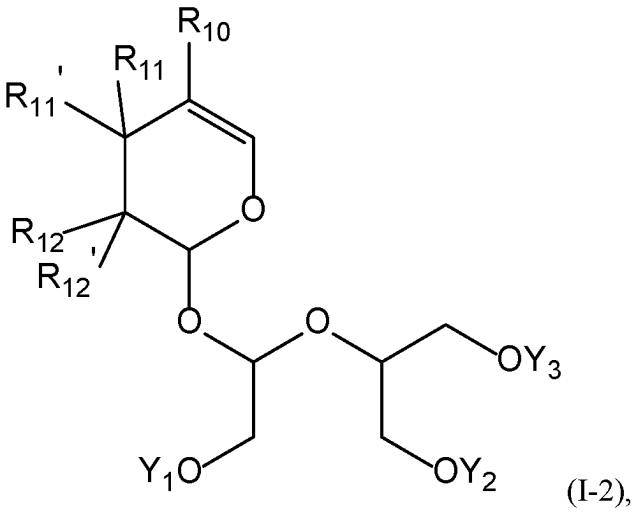
wherein:

- X is a moiety of an iridoid, a seco-iridoid or a derivative thereof, and
- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),

or a salt thereof.

[0011] In a particular embodiment, X is a moiety of aucubin, catalpol, harpagide, ajugol, geniposide, loganin, loganic acid, antirrhinoside, linarioside, feretoside, geniposidic acid, gardenoside, apodanthoside, desacetylasperulosidic acid, scandoside, methoxycinnamoyl scandoside methyl ester, demethyloleuropein, ligustroside, ligustrosidic acid, ligustaloside A, ligustaloside B, nuzhenide, secologanin, secoxyloganin, oleuropein (or equivalently "oleuropeoside"), hydroxyframoside A, hydroxyframoside B, sweroside, swertiamarin, gentiopicroside, amarogentin, or morroniside, preferably geniposide or gentiopicroside.

[0012] In a particular embodiment, said compound of formula (I) is a compound of formula (I-2):

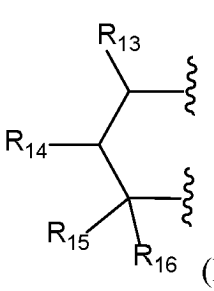
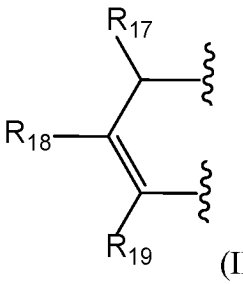
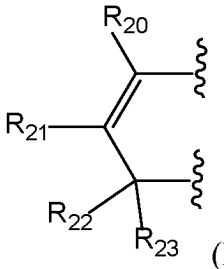
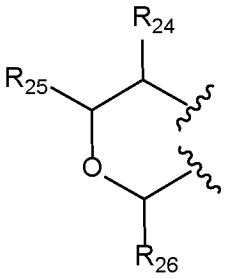


(I-2),

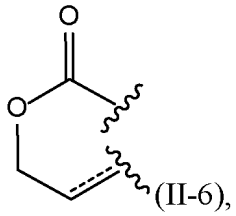
wherein:

- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),
- R_{10} is a hydrogen, -C(O)OH, or -C(O)-O-(C_1-C_{12} aliphatic group),
- R_{11} is a C_2-C_{12} aliphatic group, -CH_2-C(O)H, -CH_2-C(O)OH, or -CH_2-C(O)-O-(C_1-C_{12} aliphatic group),
- R_{11}' is a hydrogen or -OH,
- R_{12} is -CH_2-C(O)H, a C_2-C_{12} aliphatic group, -C(O)-CH_2-R_5, or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),
- R_{12}' is a hydrogen or -OH,

or R_{11} and R_{12} form together one of the chains of formula (II-2), (II-3), (II-4), or (II-5):

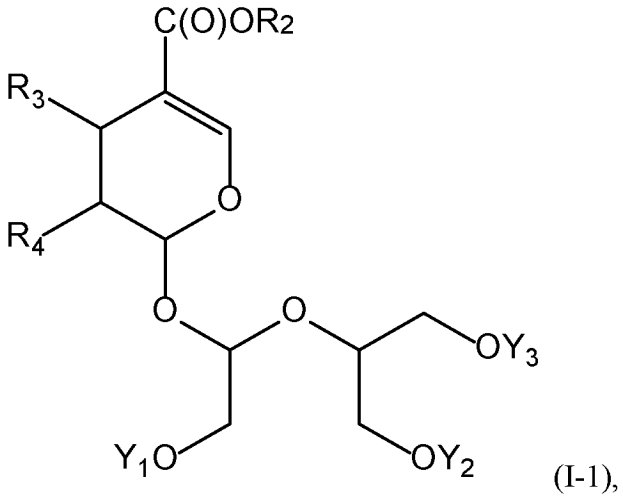

(II-2),

(II-3),

(II-4),

(II-5),

where each of R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, or R_{26} is independently a hydrogen, a halogen, -OH, -C(O)OH, -C(O)O-(C_1-C_{12} aliphatic group), -O-C(O)-(C_1-C_{12} aliphatic group), a C_1-C_{12} aliphatic group, a hydroxy-(C_1-C_{12} aliphatic group), or -CH_2-R_9', where R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),
or R_{14} and R_{15} form together a -O- group,
or R_{10} and R_{11} form together a chain of formula (II-6):


(II-6),

or R_{12} and R_{12}' form together a group of formula R_{27}-CH=, where R_{27} is a C_1-C_{12} aliphatic group, -C(O)OH, or -C(O)O-(C_1-C_{12} aliphatic group),
said aliphatic groups being each independently optionally substituted by one or more hydroxy, aryl or glycosyl derivative, said aryl being optionally substituted by one or more hydroxy or (C_1-C_6)alkoxy,
or a salt thereof.

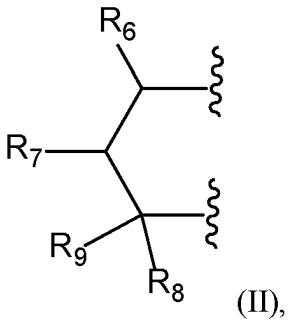
[0013] In a more particular embodiment, said compound is represented by the following formula (I-1):


(I-1),

wherein:

- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),
- R_2 is a hydrogen atom or a (C_1-C_{12}) aliphatic group,
- R_3 is -CH_2-C(O)H or -CH_2-CH_2-OH,
- R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),

or R_3 and R_4 form together the following chain of formula (II):



(II),

wherein R_6, R_7, and R_8 are each independently a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), and R_9 is a hydrogen atom or -CH_2-R_9', where R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), or a salt thereof.

[0014] In some embodiments, R_2 is a C_1-C_{12} aliphatic group, preferably a C_1-C_6 alkyl.

[0015] In some embodiments, R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), preferably a hydrogen atom, -OH or -O-C(O)-(C_1-C_6 alkyl).

[0016] In some embodiments, R_3 and R_4 form together a chain of formula (II) as defined herein wherein:

- R_6 is hydrogen; and/or
- R_7 is -OH or -O-C(O)-(C_1-C_{12} aliphatic group), preferably -OH or -O-C(O)-(C_1-C_6 alkyl); and/or
- R_8 is -OH; and/or
- R_9 is a hydrogen atom or -CH_2-R_9', where R_9' is a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl).

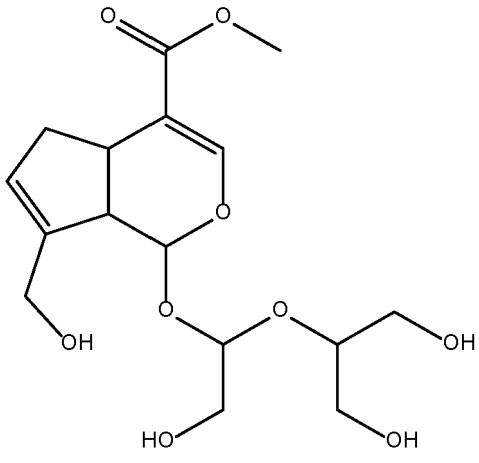
[0017] In a particular embodiment, each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-phenyl, or -C(O)-(C_1-C_6 alkyl), preferably a hydrogen or -C(O)-CH_3, more preferably a hydrogen.

[0018] In a particular embodiment, a use according to the invention is a use for tanning a hide or a skin.

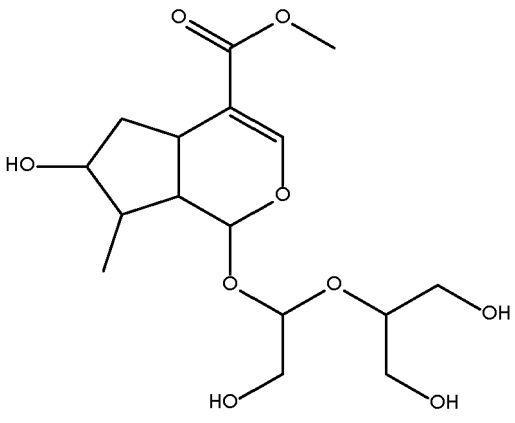
[0019] In another particular embodiment, a use according to the invention is a use in a method for manufacturing a leather or a leather substitute.

[0020] In a further particular embodiment, a use according to the invention is a use for tanning a collagen-containing material.

[0021] The present invention also relates to a compound as defined herein *per se*, with the proviso that said compound is not one of the following compounds:



(I-gen)



(I-log).

[0022] Another object of the present invention is a process for cross-linking collagen in a material comprising a step of contacting said material with a compound as defined herein. Said material may in particular be a hide or a skin.

FIGURES

[0023] Figures 1, 2, 3 and 4: Images of materials obtained after tanning of a collagen powder using compounds of the invention under various tanning conditions.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0024] The expression "C_x-C_y" in which x and y are integers, as used in the present disclosure, means that the corresponding chemical group comprises from x to y carbon atoms. If, for example, the expression C_1-C_6 is used, it means that the corresponding chemical group may comprise from 1 to 6 carbon atoms, especially 1, 2, 3, 4, 5 or 6 carbon atoms. If, for example, the expression C_2-C_5 is used, it means that the corresponding chemical group may comprise from 2 to 5 carbon atoms, especially 2, 3, 4, or 5 carbon atoms.

[0025] The term "aliphatic" refers to a saturated or unsaturated, cyclic or acyclic (preferably acyclic), linear or branched hydrocarbon chain. The expression "C_1-C_{12} aliphatic" refers to an aliphatic having 1 to 12 carbon atoms. In particular, the aliphatic may be an alkyl, an alkenyl, or an alkynyl.

[0026] The term "alkyl" refers to a saturated, linear or branched hydrocarbon chain. The expression "C_1-C_6 alkyl" refers to an alkyl having 1 to 6 carbon atoms. Examples of alkyl (or C_1-C_6 alkyl) include, for instance, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *tert*-butyl, pentyl, or hexyl.

[0027] The term "alkenyl" refers to an unsaturated, linear or branched hydrocarbon chain, having at least one carbon-carbon double bond. The expression "C_2-C_6 alkenyl" refers to an alkenyl having 2 to 6 carbon atoms. Examples of alkenyl (or C_2-C_6 alkenyl) include for instance, ethenyl, propenyl, butenyl, pentenyl, or hexenyl.

[0028] The term "alkynyl" refers to an unsaturated, linear or branched hydrocarbon chain, having at least one carbon-carbon triple bond. The expression "C_2-C_6 alkynyl" refers to an alkynyl having 2 to 6 carbon atoms. Examples of alkynyl (or C_2-C_6 alkynyl) include, for instance, ethynyl, propynyl, butynyl, pentynyl, or hexynyl.

[0029] The term "alkoxy" refers to a -O-(alkyl) group, where alkyl is as defined above. The expression "C_1-C_6 alkoxy" refers to an alkoxy having 1 to 6 carbon atoms. Examples of alkoxy (or C_1-C_6 alkoxy) include, for instance, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, *tert*-butoxy, pentoxy, or hexyloxy.

[0030] The term "aryl" refers to a mono- or bi-cyclic aromatic hydrocarbon having from 6 to 12 carbon atoms. For instance, the term "aryl" includes phenyl, biphenyl, or naphthyl. In a preferred embodiment, the aryl is a phenyl.

[0031] The term "halogen" refers to a fluorine atom, a chlorine atom, bromine atom, or iodine atom.

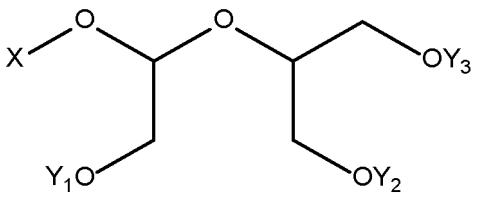
[0032] The symbol



means a single or double bond.

[0033] The "salts" of the compounds as defined herein include usual salts formed from inorganic or organic acids or bases as well as quaternary ammonium salts. More specific examples of suitable acid salts include hydrochloric, hydrobromic, sulfuric, phosphoric, nitric, perchloric, fumaric, acetic, propionic, succinic, glycolic, formic, lactic, maleic, tartaric, citric, palmoic, malonic, hydroxymaleic, phenylacetic, glutamic, benzoic, salicylic, fumaric, toluenesulfonic, methanesulfonic, naphthalene-2-sulfonic, benzenesulfonic hydroxynaphthoic, hydroiodic, malic, steroic, tannic etc. More specific examples of suitable basic salts include sodium, lithium, potassium, magnesium, aluminum, calcium, zinc salts.

[0034] The present invention relates to the use of a compound of formula (I), in a tanning process:



(I),

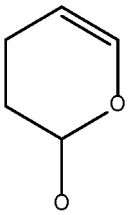
wherein:

- X is a moiety of an iridoid, a seco-iridoid or a derivative thereof, and
- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),

or a salt thereof.

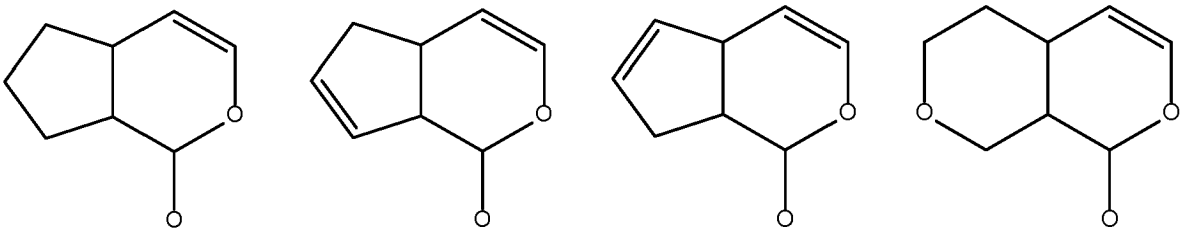
[0035] In a particular embodiment, each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-phenyl, or -C(O)-(C_1-C_6 alkyl), preferably a hydrogen or -C(O)-(C_1-C_6 alkyl), more preferably a hydrogen or -C(O)-CH_3, even more preferably a hydrogen.

[0036] A "dihydropyranyl-oxy" moiety can typically be represented as follows (said moiety being optionally substituted at any position):



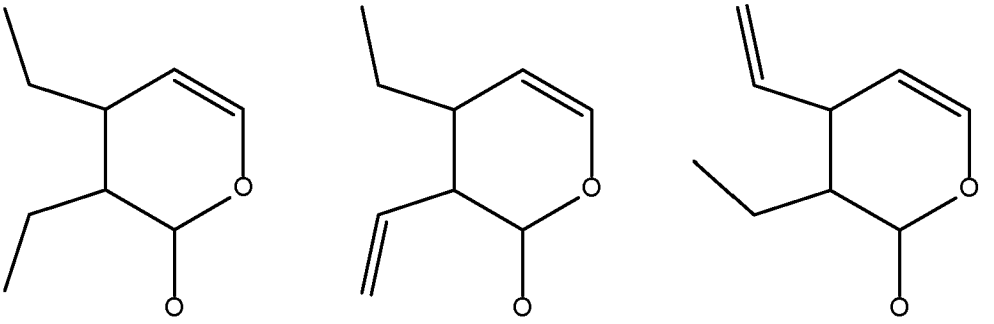
.

[0037] As used herein, an "iridoid" refers to a compound comprising a dihydropyranyl-oxy moiety, fused with a cyclopentyl, cyclopentenyl, or tetrahydropyranyl moiety. More particularly, the iridoid may comprise one of the following ring structures (each ring structure, including the oxy of the dihydropyranyl-oxy, being optionally substituted at any position):



, , , .

[0038] As used herein, a "seco-iridoid" refers to a compound comprising a dihydropyranyl-oxy moiety substituted by at least two hydrocarbon chains having each independently at least two carbons. More particularly, the seco-iridoid may comprise one of the following ring structures (each ring structure, including the at least two hydrocarbon chains and the oxy of the dihydropyranyl-oxy, being optionally substituted at any position):



, , .

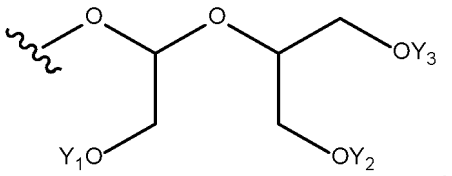
[0039] The iridoids or seco-iridoids are usually in a glycoside form (i.e. the oxy of the dihydropyranyloxy being in the form of a glucosyl group) or aglycone form (i.e. the oxy of the dihydropyranyl-oxy being in the form of a hydroxy group).

[0040] As used herein, a "moiety of an iridoid, a seco-iridoid or a derivative thereof" refers to an iridoid, a seco-iridoid or a derivative thereof, deprived of an atom or a group of atoms, while preserving the backbone of said iridoid, seco-iridoid or derivative thereof. In particular, a "moiety of an iridoid, a seco-iridoid or a derivative thereof" refers to:

- an iridoid, a seco-iridoid or a derivative thereof, deprived of a hydroxy group, when said iridoid, seco-iridoid or derivative thereof is an aglycone;
- an iridoid, a seco-iridoid or a derivative thereof, deprived of a glucosyl group, when said iridoid, seco-iridoid or derivative thereof is a glycoside.

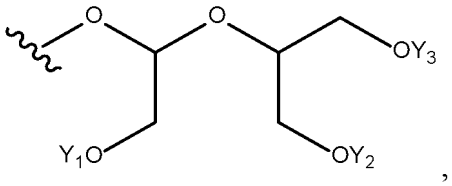
[0041] In other words, when the iridoid (or seco-iridoid or derivative thereof) is in a glycoside form, a compound of

formula (I) typically refers to the corresponding iridoid (or seco-iridoid or derivative thereof) wherein the glucosyl is formally replaced with the following moiety:



wherein Y_1, Y_2, Y_3 are as defined herein.

[0042] In other words, when the iridoid (or seco-iridoid or derivative thereof) is in an aglycone form, a compound of formula (I) typically refers to the corresponding iridoid (or seco-iridoid or derivative thereof) wherein the hydroxy is formally replaced with the following moiety:

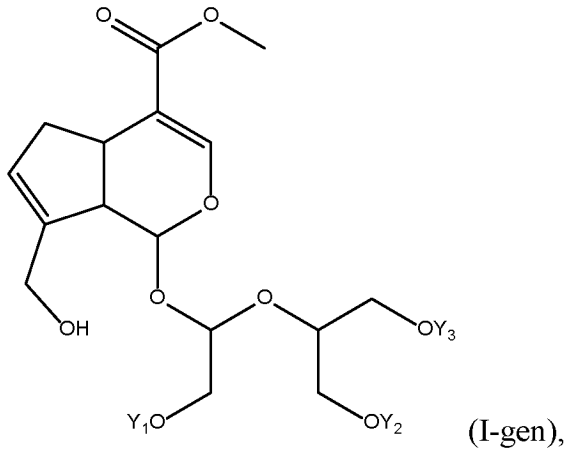


wherein Y_1, Y_2, Y_3 are as defined herein.

[0043] In a particular embodiment, X is a moiety of aucubin, catalpol, harpagide, ajugol, geniposide, loganin, loganic acid, antirrhinoside, linarioside, feretoside, geniposidic acid, gardenoside, apodanthoside, desacetylasperulosidic acid, scandoside, methoxycinnamoyl scandoside methyl ester, demethyloleuropein, ligustroside, ligustrosidic acid, ligustaloside A, ligustaloside B, nuzhenide, secologanin, secoxyloganin, oleuropein (or equivalently "oleuropeoside"), hydroxyframoside A, hydroxyframoside B, sweroside, swertiamarin, gentiopicroside, amarogentin, and morroniside.

[0044] In a preferred embodiment, X is a moiety of geniposide (or the aglycone form thereof, genipin) or a moiety of gentiopicroside (or the aglycone form thereof).

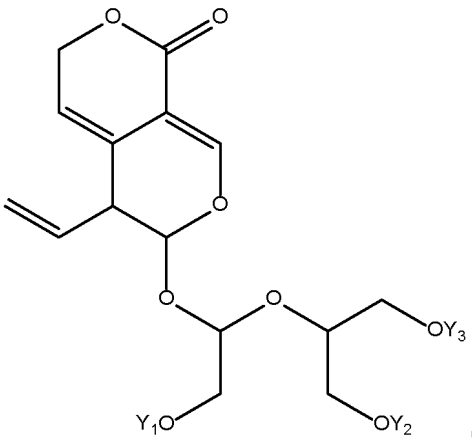
[0045] In an embodiment where X is a moiety of geniposide (or the aglycone form thereof, genipin), the compound of formula (I) can typically be represented as follows:



(I-gen),

wherein Y_1, Y_2, Y_3 are as defined herein (preferably, hydrogens).

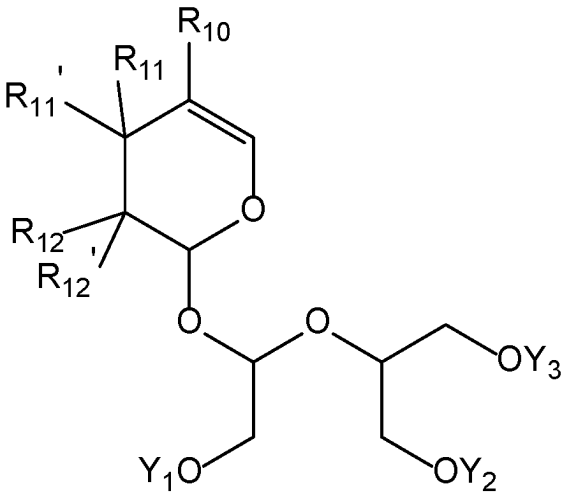
[0046] In an embodiment where X is a moiety of gentiopicroside (or the aglycone form thereof), the compound of formula (I) can typically be represented as follows:



(I-gent),

wherein Y_1, Y_2, Y_3 are as defined herein (preferably, hydrogens).

[0047] In a particular embodiment, the compound of formula (I) is a compound of formula (I-2):

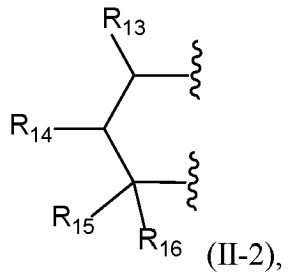


(I-2),

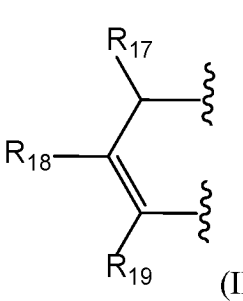
wherein:

- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),
- R_{10} is a hydrogen, -C(O)OH, or -C(O)-O-(C_1-C_{12} aliphatic group),
- R_{11} is a C_2-C_{12} aliphatic group, -CH_2-C(O)H, -CH_2-C(O)OH, or -CH_2-C(O)-O-(C_1-C_{12} aliphatic group),
- R_{11}' is a hydrogen or -OH,
- R_{12} is -CH_2-C(O)H, a C_2-C_{12} aliphatic group, -C(O)-CH_2-R_5, or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),
- R_{12}' is a hydrogen or -OH,

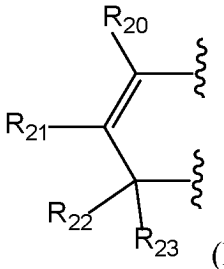
or R_{11} and R_{12} form together one of the chains of formula (II-2), (II-3), (II-4), or (II-5):



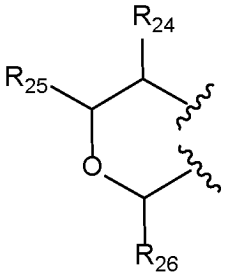
(II-2),



(II-3),

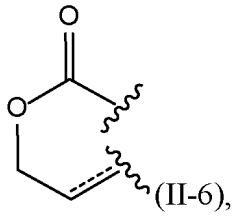


(II-4),



(II-5),

where each of R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, or R_{26} is independently a hydrogen, a halogen, -OH, -C(O)OH, -C(O)O-(C_1-C_{12} aliphatic group), -O-C(O)-(C_1-C_{12} aliphatic group), a C_1-C_{12} aliphatic group, a hydroxy-(C_1-C_{12} aliphatic group), or -CH_2-R_9', where R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),
or R_{14} and R_{15} form together a -O- group,
or R_{10} and R_{11} form together a chain of formula (II-6):



(II-6),

or R_{12} and R_{12}' form together a group of formula R_{27}-CH=, where R_{27} is a C_1-C_{12} aliphatic group, -C(O)OH, or -C(O)O-(C_1-C_{12} aliphatic group),
said aliphatic groups being each independently optionally substituted by one or more hydroxy, aryl or glycosyl derivative, said aryl being optionally substituted by one or more hydroxy or (C_1-C_6)alkoxy,
or a salt thereof.

[0048] A preferred C_1-C_{12} aliphatic group is a C_1-C_6 alkyl or a C_2-C_6 alkenyl. It is understood that this applies to C_1-C_{12} aliphatic group as such, but can also apply to any group mentioned above comprising C_1-C_{12} aliphatic group, such as -C(O)O-(C_1-C_{12} aliphatic group).

[0049] In formula (I-2), said aliphatic groups (in particular, C_1-C_{12} or C_2-C_{12} aliphatic group) are each independently optionally substituted by one or more hydroxy (preferably one or two), aryl (preferably a phenyl) or glycosyl derivative, said aryl being optionally substituted by one or more hydroxy or (C_1-C_6)alkoxy. It is understood that this applies to aliphatic group as such, but also applies to any group mentioned above comprising aliphatic group, such as -C(O)O-(C_1-C_{12} aliphatic group). An example of C_2-C_{12} aliphatic group substituted by a hydroxy is -CH_2-CH_2-OH.

[0050] In some embodiments, each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-phenyl, or -C(O)-(C_1-C_6 alkyl), preferably a hydrogen or -C(O)-(C_1-C_6 alkyl), more preferably a hydrogen or -C(O)-CH_3, even more preferably a hydrogen.

[0051] In some embodiments, R_{10} is a hydrogen, -C(O)OH, or -C(O)-O-(C_1-C_6 alkyl), wherein said C_1-C_6 alkyl is optionally substituted by a phenyl substituted one or two hydroxy.

[0052] In some embodiments, R_{11}' is a hydrogen.

[0053] In some embodiments, R_{12}' is a hydrogen.

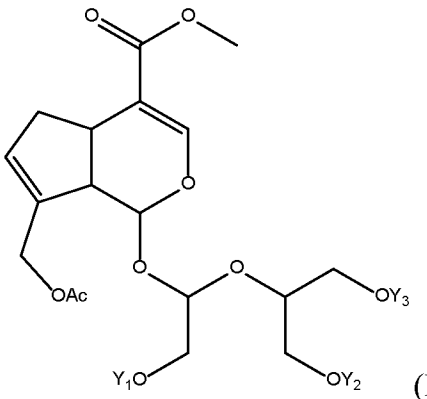
[0054] In some embodiments, R_{11} and R_{12} form together a chain of formula (II-2) as defined above, wherein each of R_{13}, R_{14}, R_{15}, and R_{16} is independently a hydrogen, a halogen (such as a chlorine), -OH, or a C_1-C_{12} aliphatic group (preferably a C_1-C_6 alkyl, such as a methyl) optionally substituted by a hydroxy,
or R_{14} and R_{15} form together a -O- group.

[0055] In an embodiment where R_{11} and R_{12} form together a chain of formula (II-2), it is preferred that at least two of R_{13}, R_{14}, R_{15}, and R_{16} are not hydrogens.

[0056] In some embodiments, R_{11} and R_{12} form together a chain of formula (II-3) as defined above, wherein each of R_{17}, R_{18}, and R_{19} is independently a hydrogen, -OH, a hydroxy-(C_1-C_6 alkyl) (such as hydroxymethyl), -C(O)-(C_2-C_6 alkenyl), said C_2-C_6 alkenyl being optionally substituted by a phenyl substituted by a methoxy.

[0057] In an embodiment where R_{11} and R_{12} form together a chain of formula (II-3), it is preferred that R_{18} is hydrogen and, R_{17} and R_{19} are not hydrogens.

[0058] In a particular embodiment, R_{11} and R_{12} form together a chain of formula (II-3) as defined above, wherein R_{17} and R_{18} are hydrogens and R_{19} is -CH_2-O-C(O)-CH_3. In such embodiment, the compound of formula (I-2) may for instance be the following compound:



(I-AcGen),

wherein Y_1, Y_2, and Y_3 are as defined herein (preferably -C(O)CH_3).

[0059] In some embodiments, R_{11} and R_{12} form together a chain of formula (II-4) as defined above, wherein each of R_{20}, R_{21}, R_{22}, and R_{23}, is independently a hydrogen, -OH, -C(O)OH, or a hydroxy-(C_1-C_{12} aliphatic group), preferably hydrogen, -OH, -C(O)OH, or hydroxy(C_1-C_6 alkyl) such as hydroxymethyl.

[0060] In an embodiment where R_{11} and R_{12} form together a chain of formula (II-4), it is preferred that R_{20} and R_{21} are hydrogens and, one or both of R_{22} and R_{23} are not hydrogens.

[0061] In some embodiments, R_{11} and R_{12} form together a chain of formula (II-5) as defined above, wherein each of R_{24}, R_{25}, or R_{26} is independently a hydrogen, -OH, or a C_1-C_{12} aliphatic group (such as a C_1-C_6 alkyl, typically a methyl), or a hydroxy-(C_1-C_{12} aliphatic group).

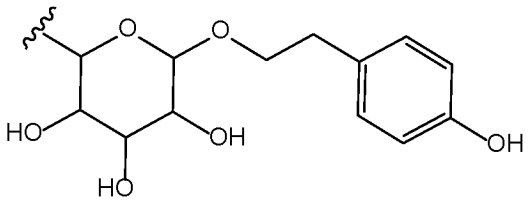
[0062] In an embodiment where R_{11} and R_{12} form together a chain of formula (II-5), it is preferred that at least two of R_{24}, R_{25}, or R_{26} are not hydrogens.

[0063] In some embodiments, R_{10} and R_{11} form together a chain of formula (II-6) as defined above. In such embodiment, it is preferred that R_{12}' is a hydrogen and R_{12} is not a hydrogen (preferably R_{12} is a C_2-C_{12} aliphatic group, more preferably a C_2-C_6 alkenyl such as an ethenyl).

[0064] In some embodiments, the compound of formula (I-2) is such that:

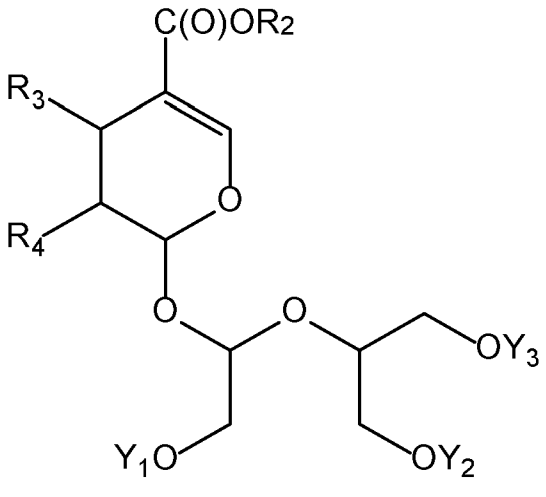
- R_{11} is a -CH_2-C(O)H, -CH_2-C(O)OH, or -CH_2-C(O)-O-(C_1-C_6 alkyl), said C_1-C_6 alkyl being optionally substituted by a glycosyl derivative or a phenyl substituted by one or two hydroxy.
- R_{12} is -CH_2-C(O)H, or a C_2-C_{12} aliphatic group (preferably a C_2-C_6 alkenyl such as an ethenyl), or R_{12} forms together with R_{12}' a group of formula R_{27}-CH=, where R_{27} is a C_1-C_{12} aliphatic group (preferably a C_1-C_6 alkyl such as a methyl), or -C(O)OH.

[0065] A particular glycosyl derivative is represented as follows:



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[0066] In a particular embodiment, a compound as defined herein is represented by the following formula (I-1):

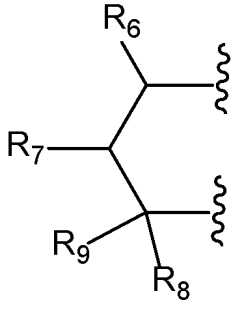


(I-1),

wherein:

- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),
- R_2 is a hydrogen atom or a (C_1-C_{12}) aliphatic group,
- R_3 is -CH_2-C(O)H or -CH_2-CH_2-OH,
- R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),

or R_3 and R_4 form together the following chain of formula (II):

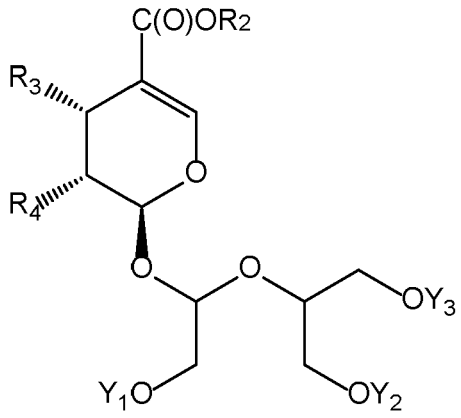


(II),

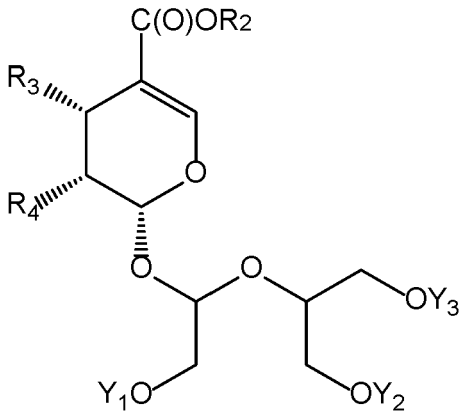
wherein R_6, R_7, and R_8 are each independently a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), and R_9 is a hydrogen atom or -CH_2-R_9', wherein R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),
or a salt thereof.

[0067] Compounds of formula (I), (I-2) or (I-1) as represented herein include all possible stereoisomers, and include not only racemic compounds but also the optically active isomers as well. The term "stereoisomer" refers to compounds which have identical molecular formulae as identified herein but which differ in the layout of their atoms in space. Stereoisomers which are not mirror images of each other, are designated as "diastereoisomers", and stereoisomers which are non-superposable mirror images of each other are designated as "enantiomers" or "optical isomers". "Stereoisomers" refer to racemates, enantiomers and diastereoisomers.

[0068] For instance, the compound of formula (I-1) as defined herein can be a compound of formula (III), a compound of formula (IV), or a mixture thereof:



(III),



(IV),

wherein, in formulae (III) and (IV):

- Y_1, Y_2, Y_3, R_2, R_3 and R_4 are as defined herein,
- when R_4 is -C(O)-CH_2-R_5, then R_5 is as defined herein,
- when R_4 is -CH(OH)-CH_2-R_5' then R_5' is as defined herein,
- when R_3 and R_4 form together said chain of formula (II), then R_6, R_7, R_8, and R_9 are as defined herein.

[0069] Preferably, the compound of formula (I-1) is a compound of formula (III) or a mixture of a compound of formula (III) and a compound of formula (IV). More preferably, a compound as defined herein is a compound of formula (III).

[0070] In a particular embodiment, each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-phenyl, or -C(O)-(C_1-C_6 alkyl), preferably a hydrogen or -C(O)-(C_1-C_6 alkyl), more preferably a hydrogen or -C(O)-CH_3, even more preferably a hydrogen.

[0071] R_2 is a hydrogen atom or a C_1-C_{12} aliphatic group. More particularly, R_2 may be a hydrogen atom or a C_1-C_6 alkyl group.

[0072] Preferably, R_2 is a C_1-C_{12} aliphatic group, more preferably a C_1-C_6 alkyl, such as a methyl.

[0073] In a particular embodiment, the compound of formula (I-1) is such that:

- R_3 is -CH_2-C(O)H or -CH_2-CH_2-OH (preferably -CH_2-C(O)H); and
- R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group).

[0074] In some embodiments, R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), preferably a hydrogen atom, -OH or -O-C(O)-(C_1-C_6 alkyl).

[0075] In a particular embodiment, R_4 is -C(O)-CH_2-R_5, where R_5 is as defined herein.

[0076] In particular, R_5 is a hydrogen atom, a C_1-C_6 alkyl group, -OH, or -O-C(O)-(C_1-C_6 alkyl group). Preferably, R_5 is a hydrogen atom or -O-C(O)-(C_1-C_{12} aliphatic group), more preferably a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl), even more preferably, a hydrogen atom or -O-C(O)-CH_3.

[0077] In another particular embodiment, R_4 is -CH(OH)-CH_2-R_5', where R_5' is as defined herein. Preferably, R_5' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl group), more preferably a hydrogen atom, -OH, or -O-C(O)-CH_3.

[0078] In a preferred embodiment, the compound of formula (I-1) is such that:

- R_3 is -CH_2-C(O)H or -CH_2-CH_2-OH; and
- R_4 is -C(O)-CH_2-R_5, where R_5 is a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl) (such as -O-C(O)-CH_3) or -CH(OH)-CH_2-R_5', where R_5' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl group) (such as -O-C(O)-CH_3).

[0079] For instance, R_3 can be -CH_2-C(O)H and R_4 can be -C(O)-CH_2-R_5, where R_5 is a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl) (such as -O-C(O)-CH_3).

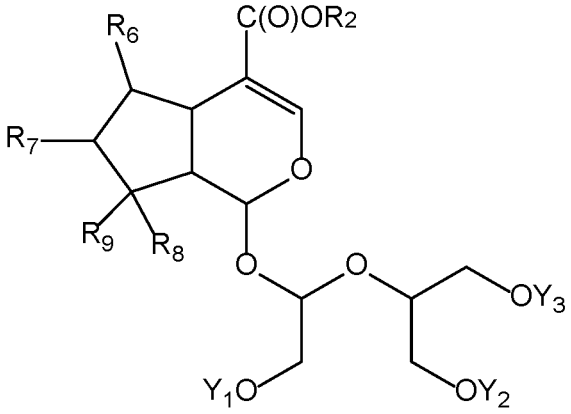
[0080] For instance, R_3 can be -CH_2-CH_2-OH and R_4 can be -CH(OH)-CH_2-R_5', where R_5' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl group) (such as -O-C(O)-CH_3).

[0081] In a more preferred embodiment, the compound of formula (I-1) is such that:

- R_2 is a C_1-C_6 alkyl group;
- R_3 is -CH_2-C(O)H or -CH_2-CH_2-OH; and

- R_4 is -C(O)-CH_2-R_5, where R_5 is a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl) (such as -O-C(O)-CH_3) or -CH(OH)-CH_2-R_5', where R_5' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl group) (such as -O-C(O)-CH_3).

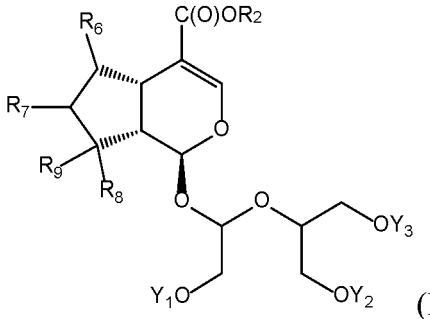
[0082] In another particular embodiment, R_3 and R_4 form together a chain of formula (II) as defined herein. In such embodiment, the compound of formula (I-1) can be represented as follows:



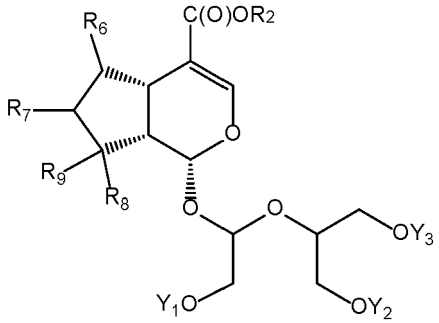
(I-II),

wherein Y_1, Y_2, Y_3, R_2, R_6, R_7, R_8, and R_9 are as defined herein.

[0083] More particularly, the stereochemistry of the compound of formula (I-II) may be as follow:



(III-II), and/or



(IV-II),

wherein Y_1, Y_2, Y_3, R_2, R_6, R_7, R_8, and R_9 are as defined herein.

[0084] Preferably, a compound as defined herein is a compound of formula (III-II) or a mixture (in particular, a racemic mixture) of a compound of formula (III-II) and a compound of formula (IV-II). More preferably, a compound as defined herein is a compound of formula (III-II).

[0085] It is understood that, in any formula represented herein, such as formula (I), (I-1), (I-2), (II), (II-2), (II-3), (II-4), (II-5), (II-6), (III), (IV), (I-II), (III-II) or (IV-II), each stereogenic center that is not defined encompasses both (R) and (S) configurations.

[0086] In a particular embodiment, R_6, R_7, and R_8 are each independently a hydrogen atom, -OH, or - O-C(O)-(C_1-C_6 alkyl group) and R_9 is a hydrogen atom or -CH_2-R_9' , where R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl group).

[0087] In a particular embodiment, at least two among R_7, R_8, and R_9 (for instance, all of R_7, R_8, and R_9) are not hydrogen atoms.

[0088] In a preferred embodiment, R_6 is hydrogen.

[0089] In a particular embodiment, R_7 is hydrogen, -OH or -O-C(O)-(C_1-C_6 alkyl), for instance hydrogen, -OH or -O-C(O)-CH_3.

[0090] In another particular embodiment, R_7 is -OH or -O-C(O)-(C_1-C_{12} aliphatic group). Preferably, R_7 is -OH or -O-C(O)-(C_1-C_6 alkyl), more preferably -OH or -O-C(O)-CH_3.

[0091] In another particular embodiment, R_7 is -O-C(O)-(C_1-C_{12} aliphatic group), for instance -C(O)-CH_3.

[0092] In a particular embodiment, R_8 is hydrogen or -OH. Preferably, R_8 is -OH.

[0093] In a particular embodiment, R_9 is a hydrogen atom.

[0094] In another particular embodiment, R_9 is -CH_2-R_9'.

[0095] In some embodiments, R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl), preferably a hydrogen atom, -OH or -O-C(O)-CH_3.

[0096] In some embodiments, R_9' is a hydrogen atom or -O-C(O)-(C_1-C_{12} aliphatic group). Preferably, R_9' is a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl), more preferably a hydrogen atom or -O-C(O)-CH_3.

[0097] In some embodiments, R_9' is -O-C(O)-(C_1-C_{12} aliphatic group), for instance -C(O)-CH_3.

[0098] In a particular embodiment, the compound of formula (I-1) (or of formula (I-II)) is such that R_3 and R_4 form together a chain of formula (II) wherein:

- R_6 is hydrogen;
- R_7 is hydrogen, -OH or -O-C(O)-(C_1-C_6 alkyl), preferably hydrogen, -OH or -O-C(O)-CH_3;
- R_8 is hydrogen or -OH; and
- R_9 is a hydrogen atom or -CH_2-R_9' , with R_9' being a hydrogen atom, -OH, or -O-C(O)-(C_1-C_6 alkyl), preferably a hydrogen atom, -OH, or -O-C(O)-CH_3.

[0099] In a more particular embodiment, the compound of formula (I-1) (or of formula (I-II)) is such that:

- R_2 is a C_1-C_6 alkyl group;
- R_3 and R_4 form together a chain of formula (II) wherein:
  - R_6 is hydrogen;
  - R_7 is hydrogen, -OH or -O-C(O)-(C_1-C_6 alkyl), preferably hydrogen, -OH or - O-C(O)-CH_3;
  - R_8 is hydrogen or -OH; and
  - R_9 is a hydrogen atom or -CH_2-R_9' , with R_9' being a hydrogen atom, -OH, or - O-C(O)-(C_1-C_6 alkyl), preferably being a hydrogen atom, -OH, or -O-C(O)-CH_3.

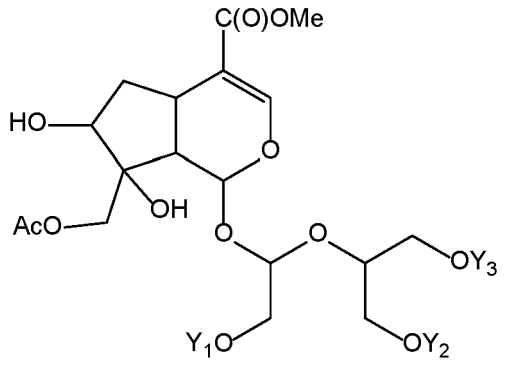
[0100] In a preferred embodiment, the compound of formula (I-1) is such that R_3 and R_4 form together a chain of formula (II) (in particular, is a compound of formula (I-II)) wherein:

- R_6 is hydrogen;
- R_7 is OH or -O-C(O)-(C_1-C_6 alkyl), preferably -OH or -O-C(O)-CH_3;
- R_8 is -OH; and
- R_9 is a hydrogen atom or -CH_2-R_9' , with R_9' being a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl), preferably being a hydrogen atom or -O-C(O)-CH_3.

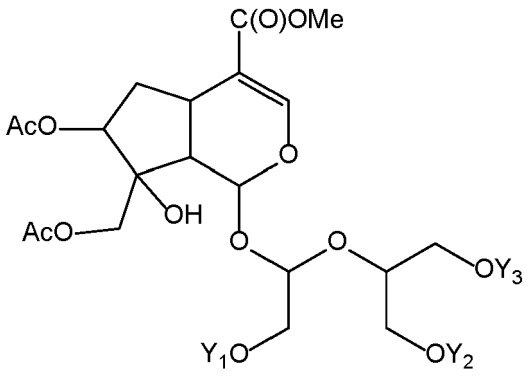
[0101] In a more preferred embodiment, the compound of formula (I-1) (or of formula (I-II)) is such that:

- R_2 is a C_1-C_6 alkyl group;
- R_3 and R_4 form together a chain of formula (II) wherein:
  - R_6 is hydrogen;
  - R_7 is OH or -O-C(O)-(C_1-C_6 alkyl), preferably -OH or -O-C(O)-CH_3;
  - R_8 is -OH; and
  - R_9 is a hydrogen atom or -CH_2-R_9' , with R_9' being a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl), preferably being a hydrogen atom or -O-C(O)-CH_3.

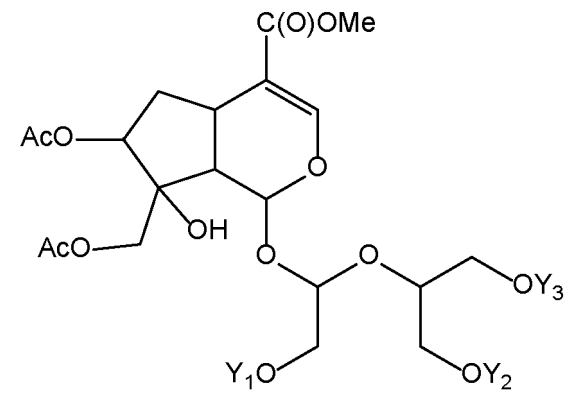
[0102] In a particular embodiment, the compound of formula (I-1) is chosen among the following compounds:



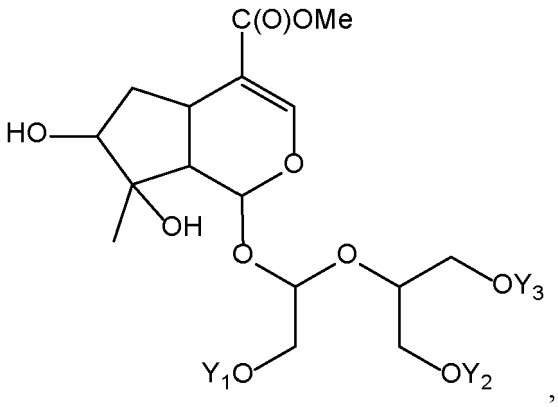
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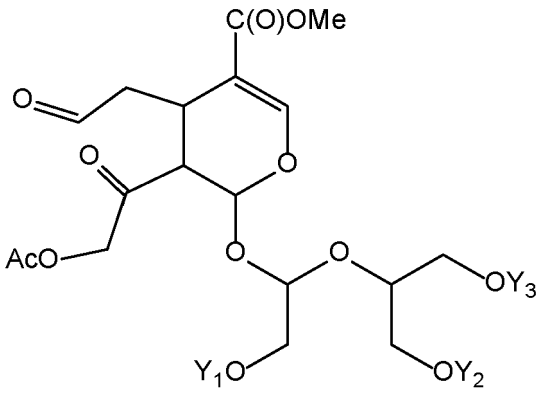
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C(O)OMe
AcO
AcO
OH
O
O
O
OY3
Y1O
OY2

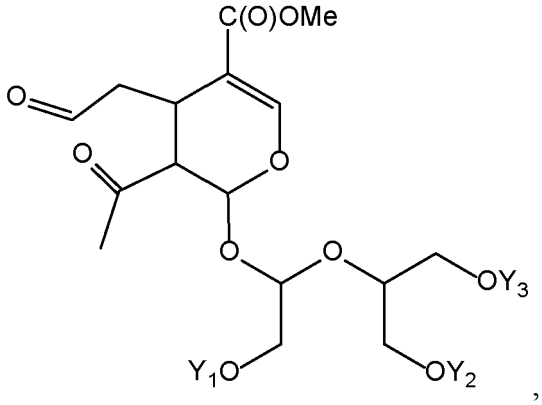
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C(O)OMe
HO
OH
O
O
O
OY3
Y1O
OY2

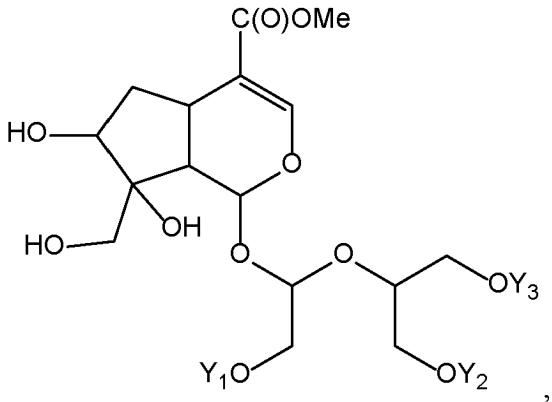
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C(O)OMe
O
O
AcO
O
O
O
OY3
Y1O
OY2

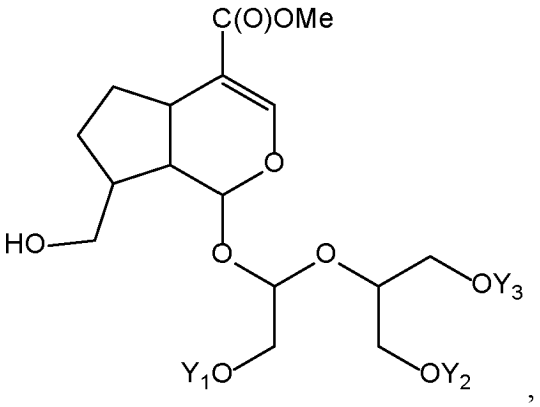
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C(O)OMe
O
O
O
O
O
OY3
Y1O
OY2

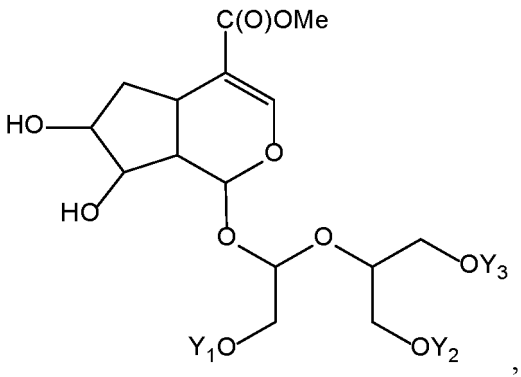
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C(O)OMe
HO
HO
OH
O
O
O
OY3
Y1O
OY2

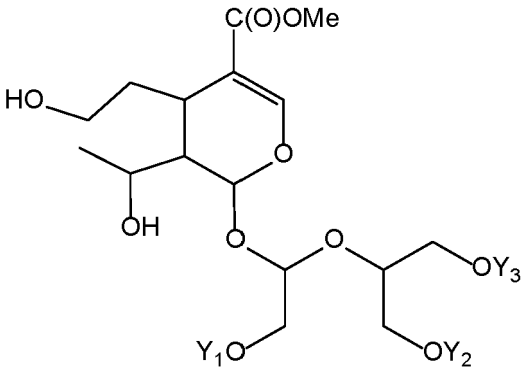
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C(O)OMe
HO
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OY3
Y1O
OY2

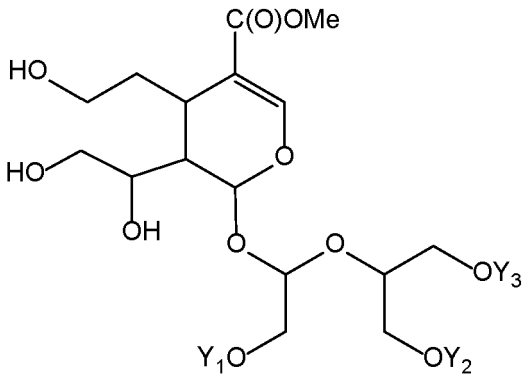
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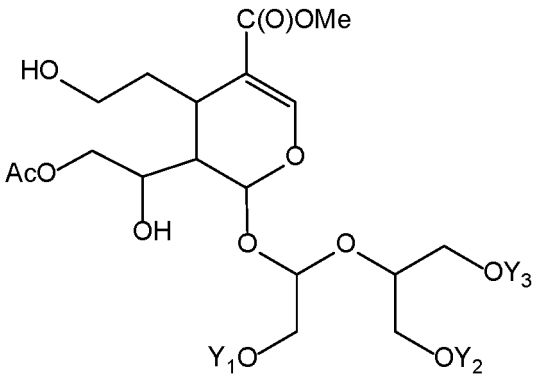

C(O)OMe
HO
HO
O
O
O
OY3
Y1O
OY2

,


C(O)OMe
HO
OH
O
O
O
OY3
Y1O
OY2

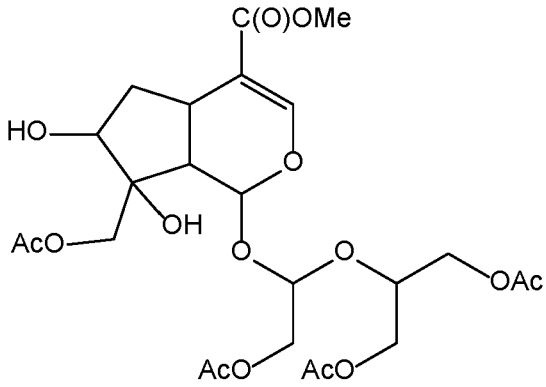
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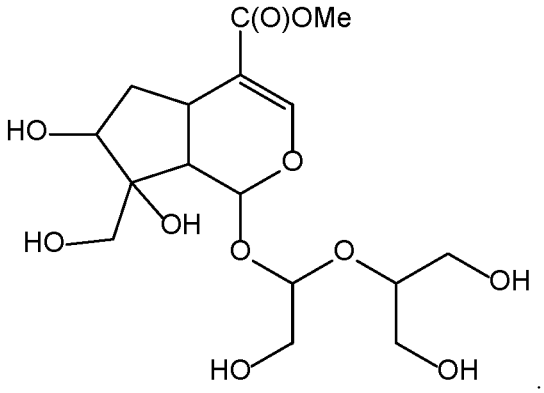


wherein Y_1, Y_2, and Y_3 are as defined herein.

[0103] For instance, the compound of formula (I-1) may be one of the following compounds:



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[0104] The compounds as defined herein (e.g. compounds of formula (I), (I-2) or (I-1)) can be prepared by any suitable technique known to the skilled artisan. In particular, the compounds as defined herein can be prepared as detailed in the examples. More specifically, such compounds may be prepared by contacting an iridoid or a seco-iridoid in its glycoside form, successively with sodium metaperiodate followed by sodium borohydride in water. Subsequent classical steps, such as hydroxylation, oxidation, reduction, or acylation can be carried out to functionalize or insert particular substituents on the iridoid or seco-iridoid.

[0105] The compounds as defined herein (e.g. compounds of formula (I), (I-2) or (I-1)) are particularly suitable for use in a tanning process, as tanning or pre-tanning agents.

[0106] Advantageously, a compound as defined herein can be activated, typically by contacting with an acid, such as hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, methanesulfonic acid, benzenesulfonic acid or *p*-toluenesulfonic acid (preferably hydrochloric acid), before and/during the tanning process. A compound as defined herein may be contacted with said acid at room temperature, preferably for a duration comprised between 30 min and 48 hours. As used herein "room temperature" refers to a temperature comprised between 15 °C and 40 °C, preferably between 20 °C and 30 °C.

[0107] The "pre-tanning" refers to a particular step of a tanning process, which is a preliminary step where a first tanning agent (i.e. "pre-tanning agent") is contacted with the collagen-containing material, e.g. the hide, before being contacted with a second tanning agent (i.e. "tanning agent"). Advantageously, the pre-tanning also enables the shaving of the leather before the second tanning agent is applied.

[0108] A tanning process may comprise or not a pre-tanning step. A compound as defined herein may be used as a pre-tanning agent and/or tanning agent in a process comprising a pre-tanning step. In such embodiment, if one among the pre-tanning agent and the tanning agent is not a compound as defined herein, it may be chosen from the group consisting of: polyphenolic extract for various vegetable, mainly gallnut, quebracho, oak, metal salt of chromium, iron, zirconium, titanium, aluminum, mainly with chloride and sulfate as counter ion, and synthetics chemicals like formol, glutaraldehyde, oxazolidine, zeolite, formol phenol (and derivate like cresol, phenol sulfonic acids) condensate, formol bisphenol (A, B, S and F) condensate, formol melamine condensate, and a mixture thereof.

[0109] A compound as defined herein may be used as a tanning agent in a tanning process not comprising a pre-tanning step.

[0110] The tanning process may in particular be a process for tanning a collagen-containing material, and more

particularly for tanning a hide or a skin.

[0111] In said tanning process, said collagen-containing material, or said hide or skin, is treated (typically, contacted) with one or more compounds as defined herein, or a composition comprising the same.

[0112] As used herein, the term "collagen" refers to naturally occurring collagens or modified collagens. The term "collagen" as used herein also refers to collagens prepared using recombinant techniques. The term collagen includes collagen, collagen fragments, collagen dispersion obtained from hide grinding and various purification steps (e.g. enzymatic or acidic hydrolysis), collagen fibers obtained through precipitation of dispersed or soluble collagen (e.g. salt, brine or ammoniac precipitation), collagen-like proteins, triple helical collagen, alpha chains, monomers, gelatin, trimers and combinations thereof. Recombinant expression of collagen and collagen-like proteins is known in the art (see in particular EP 1,232,182; US 6,428,978; US 8,188,230). In some embodiments, the collagen can be a chemically-modified collagen, a truncated collagen, unmodified or post-translationally modified, or amino acid sequence-modified collagen. In some embodiments, the collagen can be plant-based collagen. In some embodiments, a collagen solution can be fibrillated into collagen fibrils. As used herein, collagen fibrils refer to nanofibers composed of tropocollagen or tropocollagen-like structures. In some embodiments, a recombinant collagen can comprise a collagen fragment of the amino acid sequence of a native collagen molecule capable of forming tropocollagen (trimeric collagen). A recombinant collagen can also comprise a modified collagen or truncated collagen having an amino acid sequence at least 70, 80, 90, 95, 96, 97, 98, or 99% identical or similar to a native collagen amino acid sequence. In some embodiments, the collagen fragment can be a 50 kDa portion of a native collagen. Methods of producing recombinant collagen and recombinant collagen fragments are known in the art. (see in particular US 2019/0002893, US 2019/0040400, US 2019/0093116, and US 2019/0092838).

[0113] The collagen-containing material refers to a material comprising or consisting of collagen. The collagen-containing material may be from any origin, in particular from an animal (e.g. goat, bovine such as calf, cow or cattle, ovine such as sheep or lamb, reptile such as crocodile or lizard, or fish such as trout or salmon). In a particular embodiment, said collagen-containing material is a hide or a skin. The hide or skin may be from any animal, (e.g. goat, bovine such as calf, cow or cattle, ovine such as sheep or lamb, reptile such as crocodile or lizard, or fish such as trout or salmon).

[0114] The treating or contacting step may be carried out under classical conditions known to the skilled artisan. For instance, the collagen-containing material (in particular, said hide or skin) may be contacted with said one or more compounds as defined herein in an aqueous solution, optionally comprising further auxiliary agents such as, proteins, peptides, protein hydrosylates, polyamines, pH buffer, sodium chloride, sodium sulfate, sodium citrate, ammonium chloride, naphthalene sulfonic polymer, preservatives, or slippery agent.

[0115] The concentration of compound(s) as defined herein in the aqueous solution is typically comprised between 0.1 wt% and 40 wt%, preferably between 0.5% and 25%. The pH of the aqueous solution may be within a range from 1 to 15, preferably from 7 to 11. Said pH may be adjusted by using a buffer, such as a carbonate or phosphate buffer. The treating or contacting step may be carried out at a temperature comprised between 4 °C and 70 °C, preferably between 20 °C and 50 °C, more preferably between 30 °C and 40 °C. The treating or contacting step may be carried out for a duration comprised between 1 hour and 90 hours, preferably between 15 hours and 50 hours. In some embodiments, the compound(s) as defined herein may be used in a tanning process in combination with other tanning agents, such as mineral, vegetal, organic or enzymatic tanning agents (e.g. polyphenolic extract for various vegetable, mainly gallnut, quebracho, oak, metal salt of chromium, iron, zirconium, titanium, aluminum, mainly with chloride and sulfate as counter ion, and synthetics chemicals like formol, glutaraldehyde, oxazolidine, zeolite, formol phenol (and derivate like cresol, phenol sulfonic acids) condensate, formol bisphenol (A, B, S and F) condensate, formol melamine condensate, and a mixture thereof). The tanning step can be carried out in a tanning drum, a reactor or any other adapted device.

[0116] Advantageously, a compound as defined herein is contacted with an acid, such as hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, methanesulfonic acid, benzenesulfonic acid or *p*-toluenesulfonic acid (preferably hydrochloric acid), before and/or during the contacting with the collagen-containing material. Said acid is typically used in the form of an acid aqueous solution.

[0117] Particularly, a process for tanning a collagen-containing material using a compound as defined herein can comprise:

i) contacting a solution comprising a compound as defined herein with an acid, such as hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, methanesulfonic acid, benzenesulfonic acid or*p*-toluenesulfonic acid (preferably hydrochloric acid) so as to obtain a solution of a hydrolyzed compound,
ii) adjusting the solution of a hydrolyzed compound to a pH between 7 to 11, typically by adding a buffer (such as a carbonate or phosphate buffer) and
iii) contacting the resulting solution with the collagen-containing material.

[0118] Steps i), ii), and iii) can be carried out successively or simultaneously. Steps i), ii), and iii) can be carried out in any order, for instance in any one of the following orders:

- (i), (ii), and (iii); or
- (i), (iii), and (ii);
- preferably in this order i), ii), and iii).

[0119] A stabilizing salt may be added during the tanning process, for instance in the above steps (ii) or (iii), in order to prevent the degradation of the collagen-containing material which may occur under strong acid or basic conditions. Examples of such stabilizing salt include, but are not limited to, cation sulfates, cation hydrogen sulfates, cation naphthalene sulfonates, cation chloride, cation phosphate, cation citrate, cation succinate, cation tartrate, cation formate, cation acetate, cation propionate, cation sulfamate, or a mixture thereof, wherein the cation is preferably selected from the group consisting of sodium, potassium, calcium and magnesium.

[0120] In a more particular embodiment, a process for tanning a collagen-containing material using a compound as defined herein comprises:

o') contacting an iridoid, seco-iridoid, or derivative thereof in a glycoside form with sodium metaperiodate followed by sodium borohydride, so as to obtain a compound of formula (I) as defined herein,
i') contacting a solution comprising said compound of formula (I) as defined herein with an acid, such as hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, methanesulfonic acid, benzenesulfonic acid or *p*-toluenesulfonic acid (preferably hydrochloric acid) so as to obtain a solution of hydrolyzed compound,
ii') adjusting the solution of a hydrolyzed compound to a pH between 7 to 11, typically by adding a buffer (such as a carbonate or phosphate buffer), and
iii') contacting the resulting solution with the collagen-containing material.

[0121] Steps i'), ii'), and iii') can be carried out successively or simultaneously. Steps i'), ii'), and iii') can be carried out in any order, after step o'), for instance in any one of the following orders:

- (i'), (ii'), and (iii'); or
- (i'), (iii'), and (ii');
- preferably in this order i'), ii'), and iii').

[0122] A stabilizing salt as defined above may be added during the tanning process, for instance in the above steps (ii') or (iii').

[0123] In step o'), said iridoid, seco-iridoid, or derivative thereof is preferably chosen from aucubin, harpagide, catalpol, ajugol, geniposide, loganin, loganic acid, antirrhinoside, linarioside, feretoside, geniposidic acid, gardenoside, apodanthoside, desacetylasperulosidic acid, scandoside, methoxycinnamoyl scandoside methyl ester, demethyloleuropein, ligustroside, ligustrosidic acid, ligustaloside A, ligustaloside B, nuzhenide, secologanin, secoxyloganin, oleuropein, hydroxyframoside A, hydroxyframoside B, sweroside, swertiamarin, gentiopicroside, amarogentin, and morroniside, preferably geniposide or gentiopicroside.

[0124] Advantageously, compounds as defined herein have a low toxicity, in particular compared with the aglycone form of iridoids or seco-iridoids. Compounds as defined herein advantageously have a median lethal dose (LD_{50}) higher than that of the corresponding aglycone form. Compounds as defined herein may also allow to obtain a high-quality leather or leather substitute. In particular, said leather or leather substitute may:

- be colorless or slightly colored (for instance, yellow, orange, beige), and/or
- have a shrinkage temperature of at least 65°C (for instance from 65°C to 90°C), or at least 70 °C (for instance, from 70°C to 85°C), as measured by DSC, and/or
- have a high-quality grain and leather surface.

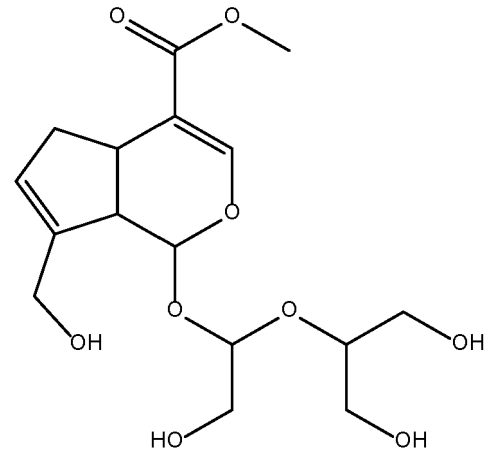
[0125] The shrinkage temperature may in particular be suitable to shave leather and to prepare the step of tanning (i.e. the step subsequent to the pre-tanning, if present in the tanning process). The high-quality grain and leather surface may in particular be suitable for aniline finishing, and be characterized by a very low shrinking of the grain.

[0126] Compounds as defined herein are used in a method for manufacturing a leather or leather substitute. A "leather substitute" refers typically to a material having similar properties as leather, and obtained by a tanning process applied to a substitute of an animal skin or hide. Said leather or leather substitute can be used in the fashion, accessories, household's appliances and other furniture industries, and especially for manufacturing bags, shoes, watch straps, belts or wallets.

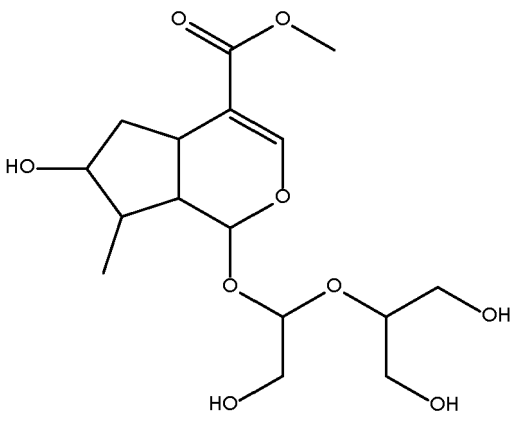
[0127] Another object of the present invention is a process for cross-linking collagen in a material comprising a step of contacting said material with a compound as defined herein. Said material may in particular be a hide or skin.

[0128] Another object of the present invention is a compound as defined herein (e.g. compounds of formula (I), (I-2) or

(I-1)) *per se,* with the proviso that said compound is not one of the following compounds (including any stereoisomer thereof):



(I-gen)



(I-log).

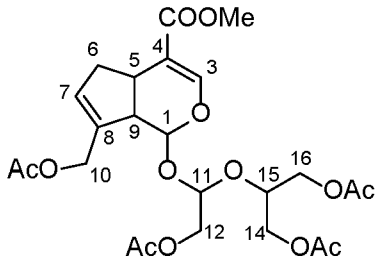
[0129] In particular, said compound *per se* is a compound of formula (I) as defined herein, with the proviso that X is not a moiety of geniposide or loganin (or the aglycone form thereof).

[0130] The invention will also be described in further detail in the following examples, which are not intended to limit the scope of this invention, as defined by the attached claims.

EXAMPLES

Example 1. Preparation of iridoid derivatives of formula (I)

[0131]



1

[0132] Sodium metaperiodate (1.15 g, 5.3 mmol, 2 eq) was added to a solution of geniposide (1 g, 2.6 mmol) in water (7 mL) and the mixture was stirred at room temperature. After 2 hours, the reaction mixture was cooled to 0 °C. Sodium borohydride (0.4 g, 10.8 mmol, 4 eq) was carefully added and the mixture was stirred at room temperature. After 2 h, water was evaporated under reduced pressure to obtain a white solid which was stirred in an acetic anhydride/pyridine mixture (1:1, 20 mL) overnight. Solvents were then evaporated under reduced pressure to give an orange solid which was dissolved in EtOAc (30 mL). The organic layer was washed with HCl aqueous solution (1 M), a saturated aqueous solution of $NaHCO_3$ and brine. The organic layer was then dried over $MgSO_4$ and evaporated under reduced pressure to give a yellow liquid which was purified by silica gel chromatography (cyclohexane/ethyl acetate 65/35) to afford compound **1** (1.18 g, 2.2 mmol, 87%) as a yellow oil.

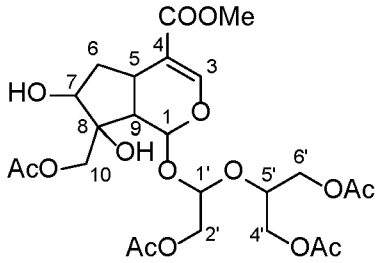
[0133] **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 7.44 (d, J = 1.3 Hz, 2H, H-3, H-3'), 5.90 (br s , 1H, H-7'), 5.86 (br s , 1H, H-7), 5.28-5.19 (m, 2H, H-11, H-11'), 5.09-5.01 (m, 2H, H-1, H-1'), 4.82 (br s, 2H, H-10_a', H-10_b'), 4.71 (br s, 2H, H-10_a, H-10_b), 4.30-3.98 (m, 14H, H-12_a, H-12_b, H-12_a', H-12_b', H-14_a, H-14_b, H-14_a', H-14_b', H-15, H-15', H-16_a, H-16_b, H-16_a', H-16_b'), 3.72 (s, 3H, OMe), 3.24 (q, J = 7.8 Hz, 1H, H-5), 2.96-2.81 (m, 2H, H-6_a, H-6_a'), 2.81-2.71 (m, 2H, H-9, H-9'), 2.24-2.21 (m, 1H, H-6_b), 2.08 (s, 6H, CH_3-C=O), 2.07 (12H, s, CH_3-C=O), 2.04 (6H, s, CH_3-C=O).

[0134] **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm) 170.6 (C=O), 169.4 (C=O), 167.3 (C=O), 151.4 (C-3), 151.4 (C-3'), 137.7 (C-4), 137.0 (C-4), 132.0 (C-7'), 131.3 (C-7), 111.8 (C-8), 98.0 (C-11, C-11'), 96.4 (C-1), 74.2 (C-15), 64.5 (C-12), 63.6 (C-14, C-16), 62.2 (C-10), 61.7 (C-10'), 51.4 (O=C-O-CH_3), 46.4 (C-9), 46.3 (C-9'), 38.8 (C-6), 35.0 (C-5), 21.0

($\underline{C}H_3$-C=O), 20.8 ($\underline{C}H_3$-C=O, $\underline{C}H_3$-C=O), 20.7 ($\underline{C}H_3$-C=O).

[0135] **HRMS** (ESI) *m/z*: calculated for $C_{24}H_{32}O_{13}Na$ $[M + Na]^+$ 551.1741 ; found 551.1730.

[0136] R_f = 0.33 (SiO_2, cyclohexane/AcOEt 65/35).



2

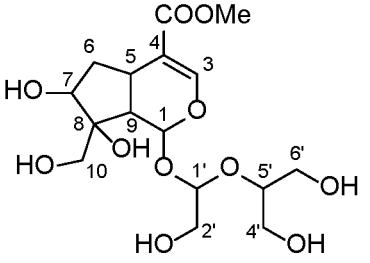
[0137] Potassium carbonate (680 g, 4.9 mmol, 3 eq), potassium ferricyanide (III) (2.7 g, 8.2 mmol, 5 eq), potassium osmate(VI) dihydrate (0.024 g, 0.06 mmol, 0.04 eq), and quinuclidine (0.015 g, 0.13 mmol, 0.08 eq) were suspended in THF/ H_2O (2/1, 12 mL). After 5 min of stirring, a solution of **1** (866 g, 1.6 mmol) in THF (4 mL) was added to the reaction mixture. The dark suspension was vigorously stirred at room temperature overnight and sodium sulfite (1 g, 8.2 mmol, 5 eq) was introduced. After 20 min, ethyl acetate (20 mL) was added and the mixture was vigorously stirred 2h. After filtration over a pad of celite, the aqueous layer was extracted with EtOAc. Combined organic layers were washed with HCl aqueous solution (1M), saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The obtained yellow oil was purified by silica gel chromatography (cyclohexane/ethyl acetate 1/3) to afford compound **2** as a yellow oil (530 g, 0.93 mmol, 59 %).

[0138] **^{1}H NMR** (300 MHz, *$CDCl_3$*) δ(ppm) 7.31 (d, *J* = 0.7 Hz, 1H, H-3), 5.55 (d, *J* = 2.2 Hz, 1H, H-1), 5.18-5.09 (m, 1H, H-11), 4.30-3.91 (m, 10H, H-7, H-10_a, H-10_b, H-12_a, H-12_b, H-14_a, H-14_b, H-16_a, H-16_b,) 3.72 (s, 3H, OMe), 3.25-3.10 (m, 1H, H-5), 2.77 (dd, *J* = 10.1 Hz, *J* = 2.2 Hz, 1H, H-9), 2.37-2.24 (m, 1H, H-6_a), 2.09 (6H, s, $\underline{C}H_3$-C=O), 2.08 (3H, s, CH_3-C=O), 2.03 (3H, s, CH_3-C=O), 1.90-1.74 (m, 1H, H-6_b).

[0139] **^{13}C NMR** (75 MHz, *$CDCl_3$*) δ (ppm) 171.2 ($\underline{C}$=O), 171.1 ($\underline{C}$=O), 170.9 ($\underline{C}$=O), 170.5 ($\underline{C}$=O), 166.9 ($\underline{C}$=O), 149.6 (C-3), 97.8 (C-11), 93.3 (C-1), 79.9 (C-8), 74.0 (C-7), 73.5 (C-15), 66.2 (C-10), 64.2 (C-12), 63.6 (C-14, C-16), 51.4 (O=C-O-$\underline{C}H_3$), 47.9 (C-9), 37.0 (C-6), 26.9 (C-5), 20.9 ($\underline{C}H_3$-C=O, CH_3-C=O), 20.8 ($\underline{C}H_3$-C=O), 20.6 ($\underline{C}H_3$-C=O).

[0140] **HRMS** (ESI) *m/z*: calculated for $C_{24}H_{34}O_{15}Na$ $[M + Na]^+$ 585.1795 ; found 585.1794.

[0141] R_f = 0.25 (SiO_2, cyclohexane/AcOEt 1/3).



3

[0142] To a stirred solution of **2** (1.32 g, 2.3 mmol) in anhydrous MeOH (25 mL) at 0 °C was added a 0.65 M solution of MeONa in MeOH (1.1 mL, 0.7 mmol, 0.3 eq). After 20 min at room temperature, the solution was neutralized with Dowex X50 ion exchange resin, filtrated and evaporated under reduced pressure to afford **3** (900 mg, 2.3 mmol, 100%) as an uncoloured oil without further purification.

[0143] **^{1}H NMR** (300 MHz, *Methanol-d4*) δ (ppm) 7.40 (d, *J* = 0.9 Hz, 1H, H-3), 5.71 (d, *J* = 4.1 Hz, 1H, H-1), 5.18-5.09 (t, J= 5.0 Hz, 1H, H-11), 3.97 (dd, *J* = 6.4 Hz, *J* = 5.0 Hz, 1H, H-7), 3.80-3.50 (m, 12H, H-10_a, H-10_b, H-12_a, H-12_b, H-14_a, H-14_b, H-15, H-16_a, H-16_b, CH_3-C=O) 3.13 (td, *J* = 9.3 Hz, *J* = 6.0 Hz, 1H, H-5), 2.52 (dd, *J* = 9.3 Hz, *J* = 4.1 Hz, 1H, H-9), 2.19 (ddd, *J* = 14.0 Hz, *J* = 9.3 Hz, *J* = 5.0 Hz, 1H, H-6_a), 1.77 (td, *J* = 14.1 Hz, *J* = 6.4 Hz, 1H, H-6_b)

[0144] **^{13}C NMR** (75 MHz, *Methanol-d4*) δ (ppm) 166.0 ($\underline{C}$=O), 151.9 (C-3), 113.7 (C-4) 101.8 (C-11), 94.6 (C-1), 82.4 (C-11), 82.4 (C-8), 74.1 (C-7), 65.3 (C-10), 64.7 (C-12), 63.4 ppm (C-14), 63.2 (C-16), 51.7 (O=C-O-$\underline{C}H_3$), 49.2 (C-9), 38.9 (C-6), 29.1 (C-5).

[0145] **HRMS** (ESI) *m/z*: calculated for $C_{16}H_{26}O_{11}Cl$ $[M + Cl]^-$ 429.1164; found 429.1143.

Example 2. Tanning process using iridoid derivatives of formula (I)

[0146] In a brown vial, a solution of iridoid derivative (17 mg, 8.5% w/w) in 2M aqueous HCl (0.17 mL) was stirred at room temperature during 1h and then diluted in a carbonate buffer (pH 9 ; 3 mL, 1500% w/w). Collagen powder (200 mg) was added after 24 hours of rehydration in ultra-pure water (3mL). The vial was heated at 37 °C for 48 hours with moderate stirring. The collagen powder was finally filtered and thoroughly rinsed with ultrapure water (ca. 20 mL).

[0147] The impact of the time of acid hydrolysis (Tables 1, 2 and 3), the tanning agent content (Table 4), and the pH of hydrolysis (Table 5) on the tanning process were assessed by measuring shrinkage temperatures. Reference collagen powder had a shrinkage temperature of 60°C. Shrinkage temperatures were determined by Differential Scanning Calorimetry (DSC). The temperatures shown in Tables 1-5 below are average values.

Table 1

Entry	Iridoid derivative	Acid Hydrolysis time	Shrinkage Temperature	Colour of the collagen powder
1	Compound **1**	4h	68 °C	Violet

Table 2

Entry	Iridoid derivative	Acid Hydrolysis time	Shrinkage Temperature	Colour of the collagen powder
1	Compound **2**	2 h	68 °C	Pale yellow
2	Compound **2**	4 h	71 °C	Yellow
3	Compound **2**	6 h	73 °C	Yellow
4	Compound **2**	9 h	76 °C	Yellow
5	Compound **2**	24 h	76 °C	Yellow

Table 3

Entry	Iridoid derivative	Acid hydrolysis time	Shrinkage Temperature	Colour of the collagen powder
1	Compound **3**	0.5 h	75 °C	Pale yellow
2	Compound **3**	1 h	76 °C	Pale yellow
3	Compound **3**	2 h	76 °C	Pale yellow
4	Compound **3**	4 h	77 °C	Yellow
5	Compound **3**	8 h	77 °C	Yellow
6	Compound **3**	24 h	75 °C	Yellow

Table 4

Entry	Iridoid derivative	Tanning agent content (w/w)	Shrinkage Temperature	Colour of the collagen powder
1	Compound **3**	8.5 %	76 °C	Pale yellow
2	Compound **3**	17 %	77 °C	Yellow
3	Compound **3**	34%	77 °C	Yellow

Table 5

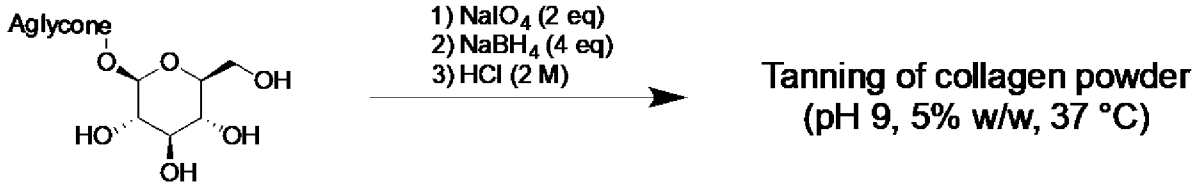
Entry	Iridoid derivative	Acid hydrolysis time and pH	Shrinkage Temperature	Colour of the collagen powder
1	Compound **3**	pH 0 ; 4 h	73 °C	Yellow
2	Compound **3**	pH 0 ; 4 h	74 °C	Yellow
3	Compound **3**	pH 1 ; 24 h	70 °C	Pale yellow

[0148] These experiments (Tables 1-5, Figures 1-3) show that the iridoid derivatives can be effectively used in a tanning process, under various conditions. Good shrinkage temperatures of at least ~ 70 °C and up to 77 °C were obtained, by using a moderate amount of iridoid derivative and especially when using sufficient acidic conditions and time during the

hydrolysis step.

Example 3. Direct tanning process using iridoid derivatives of formula (I)

[0149]

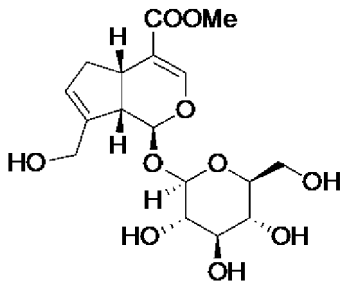


[0150] Sodium metaperiodate (220 mg, 1 mmol, 2 eq) was added to a solution of the iridoid glycoside (0.5 mmol) in water (1.4 mL) and the mixture was stirred at room temperature for 2 h. After the reaction mixture was cooled to 0 °C, sodium borohydride (78 mg, 2 mmol, 4 eq) was carefully added and the mixture was stirred at room temperature for 2 h, and then 6 M hydrochloric acid (0.7 mL, 4.2 mmol, 8.4 eq) was added for the acid hydrolysis step.

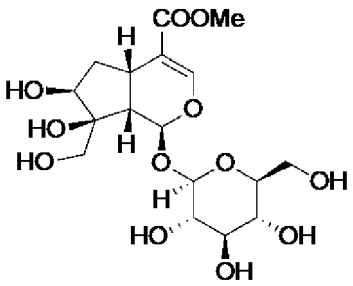
[0151] After 1 hour, the hydrolysate (0.17 mL) was diluted in a carbonate buffer of pH 9 (3 mL, 1500 % w/w) in a brown vial. Collagen powder (200 mg) was added after 24 hours of rehydration in ultra-pure water (3mL). The vial was heated at 37 °C for 48 hours with moderate stirring. The collagen powder was finally filtered and thoroughly rinsed with ultrapure water (ca. 20 mL).

[0152] The impact of the iridoid derivative (Table 6), the time of hydrolysis (Table 7), the amount of sodium metaperiodate and sodium borohydride (Table 8) on the tanning process were assessed by measuring shrinkage temperatures. Shrinkage temperatures were determined by Differential

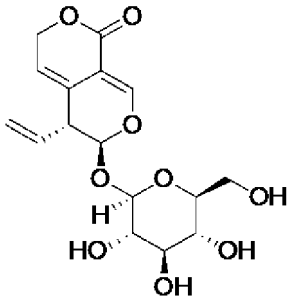
[0153] Scanning Calorimetry (DSC). The temperatures shown in Tables 6-8 below are average values.



Geniposide



Dihydroxylated geniposide



Gentiopicroside

Table 6

Entry	Iridoid glycoside	Shrinkage Temperature	Colour of the collagen powder
1	Geniposide	84 °C	Dark blue
2	Dihydroxylated geniposide	78 °C	Pale yellow
3	Gentiopicroside	84 °C	Orange

Table 7

Entry	Iridoid glycoside	Hydrolysis time	Shrinkage Temperature	Colour of the collagen powder
1	Geniposide	15 minutes	80 °C	Dark blue
2	Geniposide	60 minutes	84 °C	Dark blue
3	Geniposide	120 minutes	83 °C	Dark blue

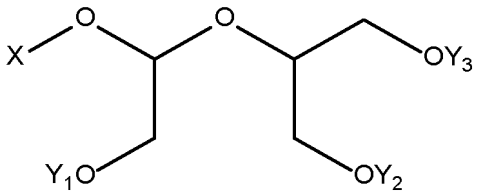
Table 8

Entry	Iridoid glycoside	Equivalents	Shrinkage Temperature	Colour of the collagen powder
1	Dihydroxylated geniposide	$NaIO_4$ (2 eq) $NaBH_4$ (4 eq)	75 °C	Pale yellow
2	Dihydroxylated geniposide	$NaIO_4$ (4 eq) $NaBH_4$ (8 eq)	78 °C	Pale yellow

[0154] These experiments (Tables 6-8, Figure 4) demonstrate that the iridoid derivatives can be effectively used in a direct tanning process (namely without being isolated after conversion of the glycoside), under various conditions. Good shrinkage temperatures of at least 75 °C and up to 84 °C were obtained.

Claims

1. Use of a compound of formula (I), in a tanning process:



(I),

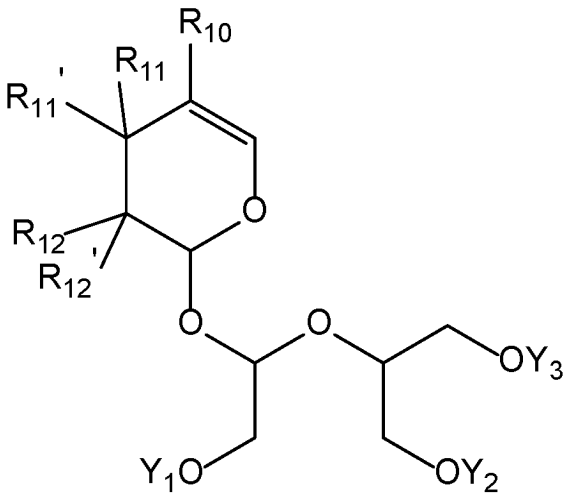
wherein:

- X is a moiety of an iridoid, a seco-iridoid or a derivative thereof, and
- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),

or a salt thereof.

2. Use according to claim 1, wherein X is a moiety of aucubin, harpagide, catalpol, ajugol, geniposide, loganin, loganic acid, antirrhinoside, linarioside, feretoside, geniposidic acid, gardenoside, apodanthoside, desacetylasperulosidic acid, scandoside, methoxycinnamoyl scandoside methyl ester, demethyloleuropein, ligustroside, ligustrosidic acid, ligustaloside A, ligustaloside B, nuzhenide, secologanin, secoxyloganin, oleuropein, hydroxyframoside A, hydroxyframoside B, sweroside, swertiamarin, gentiopicroside, amarogentin, or morroniside, preferably geniposide or gentiopicroside.

3. Use according to claim 1, wherein said compound is represented by the following formula (I-2):

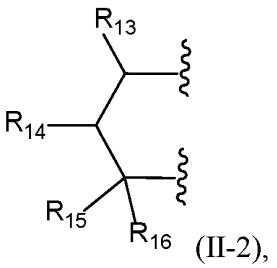


(I-2),

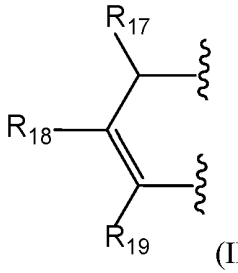
wherein:

- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),
- R_{10} is a hydrogen, -C(O)OH, or -C(O)-O-(C_1-C_{12} aliphatic group),
- R_{11} is a C_2-C_{12} aliphatic group, -CH_2-C(O)H, -CH_2-C(O)OH, or -CH_2-C(O)-O-(C_1-C_{12} aliphatic group),
- R_{11}' is a hydrogen or -OH,
- R_{12} is -CH_2-C(O)H, a C_2-C_{12} aliphatic group, -C(O)-CH_2-R_5, or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),
- R_{12}' is a hydrogen or -OH,

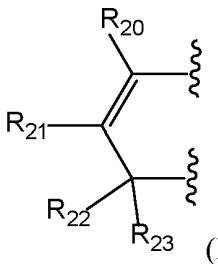
or R_{11} and R_{12} form together one of the chains of formula (II-2), (II-3), (II-4), or (II-5):



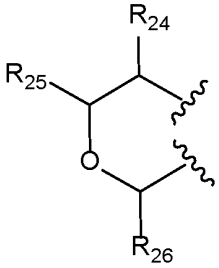
(II-2),



(II-3),



(II-4),

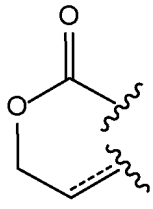


(II-5),

where each of R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, or R_{26} is independently a hydrogen, a halogen, -OH, -C(O)OH, -C(O)O-(C_1-C_{12} aliphatic group), -O-C(O)-(C_1-C_{12} aliphatic group), a C_1-C_{12} aliphatic group, a hydroxy-(C_1-C_{12} aliphatic group), or -CH_2-R_9', where R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),

or R_{14} and R_{15} form together a -O- group,

or R_{10} and R_{11} form together a chain of formula (II-6):



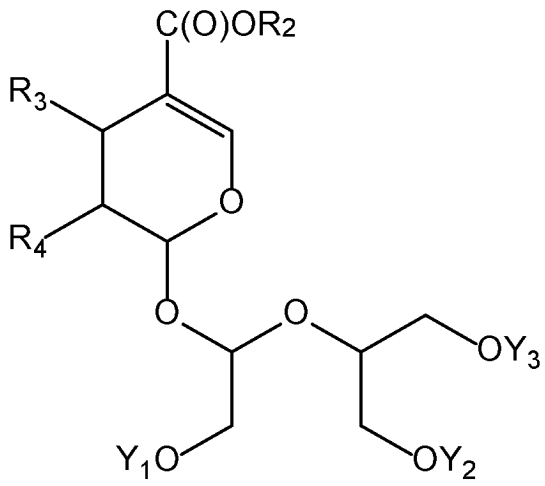
(II-6),

or R_{12} and R_{12}' form together a group of formula R_{27}-CH=, where R_{27} is a C_1-C_{12} aliphatic group, -C(O)OH, or -C(O)O-(C_1-C_{12} aliphatic group),

said aliphatic groups being each independently optionally substituted by one or more hydroxy, aryl or a glycosyl derivative, said aryl being optionally substituted by one or more hydroxy or (C_1-C_6)alkoxy,

or a salt thereof.

4. Use according to claim 3, wherein said compound is represented by the following formula (I-1):

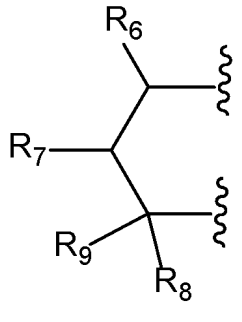


(I-1),

wherein:

- each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-aryl, or -C(O)-(C_1-C_{12} aliphatic group),
- R_2 is a hydrogen atom or a (C_1-C_{12}) aliphatic group,
- R_3 is -CH_2-C(O)H or -CH_2-CH_2-OH,
- R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, a C_1-C_{12} aliphatic group, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group),

or R_3 and R_4 form together the following chain of formula (II):



(II),

wherein R_6, R_7, and R_8 are each independently a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), and R_9 is a hydrogen atom or -CH_2-R_9', wherein R_9' is a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), or a salt thereof.

5. Use according to claim 4, wherein R_2 is a C_1-C_{12} aliphatic group, preferably a C_1-C_6 alkyl.

6. Use according to claim 4 or 5, wherein R_4 is -C(O)-CH_2-R_5 or -CH(OH)-CH_2-R_5', where R_5 and R_5' are each independently a hydrogen atom, -OH, or -O-C(O)-(C_1-C_{12} aliphatic group), preferably a hydrogen atom, -OH or -O-C(O)-(C_1-C_6 alkyl).

7. Use according to one of claims 4 to 6, wherein R_3 and R_4 form together the following chain of formula (II) wherein:

- R_6 is hydrogen; and/or
- R_7 is -OH or -O-C(O)-(C_1-C_{12} aliphatic group), preferably -OH or -O-C(O)-(C_1-C_6 alkyl); and/or
- R_8 is -OH; and/or
- R_9 is a hydrogen atom or -CH_2-R_9', with R_9' being a hydrogen atom or -O-C(O)-(C_1-C_6 alkyl).

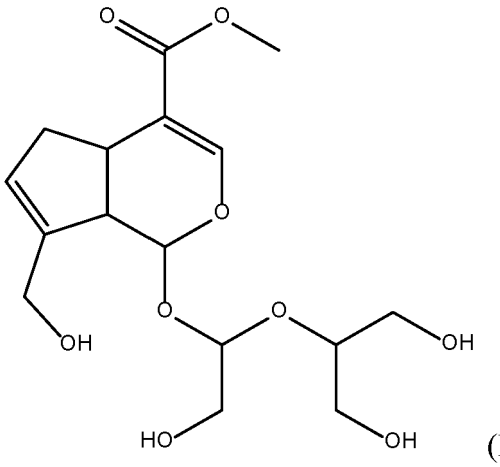
8. Use according to any one of claims 1 to 7, wherein each of Y_1, Y_2, and Y_3 is independently a hydrogen, -C(O)-phenyl, or -C(O)-(C_1-C_6 alkyl), preferably a hydrogen or -C(O)-CH_3, more preferably a hydrogen.

9. Use according to any one of claims 1 to 8, for tanning a hide or a skin.

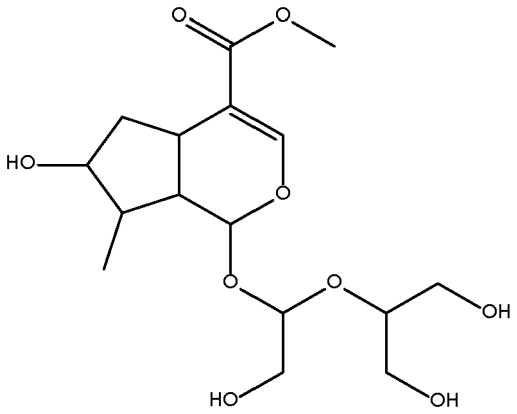
10. Use according to any one of claims 1 to 8, for tanning a collagen-containing material.

11. A method for manufacturing a leather or a leather substitute, the method comprising the use according to any one of claims 1 to 8.

12. A compound as defined in any one of claims 1 to 8, with the proviso that said compound is not one of the following compounds:



(I-gen)



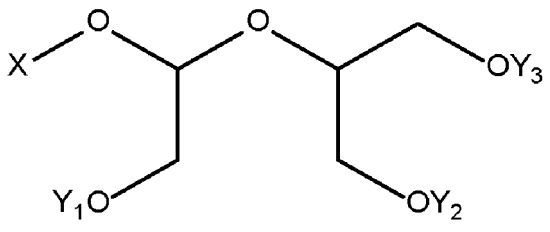
(I-log).

13. A process for cross-linking collagen in a material comprising a step of contacting said material with a compound as defined in any one of claims 1 to 8, and 12.

14. The process according to claim 13, wherein said material is a hide or a skin.

Patentansprüche

1. Verwendung einer Verbindung der Formel (I), in einem Gerbverfahren:



(I),

wobei:

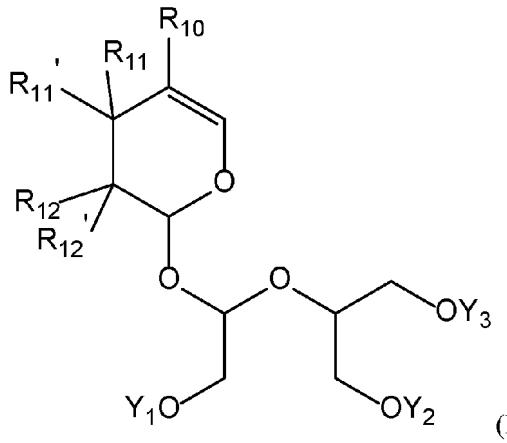
- X ein Rest eines Iridoids, eines Seco-Iridoids oder eines Derivats davon ist, und
- Y_1, Y_2 und Y_3 jeweils unabhängig ein Wasserstoff, -C(O)-Aryl oder -C(O)-(C_1-C_{12} aliphatische Gruppe) ist,

oder ein Salz davon.

2. Verwendung nach Anspruch 1, wobei X ein Rest von Aucubin, Harpagid, Catalpol, Ajugol, Geniposid, Loganin, Logansäure, Antirrhinosid, Linariosid, Feretosid, Geniposidische Säure, Gardenosid, Apodanthosid, Desacetylasperulosidsäure, Scandosid, Methoxyzimtsäure-Scandosid-Methylester, Demethyloleuropein, Ligustrosid, Ligust-

rosidensäure, Ligustalosid A, Ligustalosid B, Nuzhenid, Secologanin, Secoxyloganin, Oleuropein, Hydroxyframosid A, Hydroxyframosid B, Swerosid, Swertiamarin, Gentiopicrosid, Amarogentin oder Morronisid, vorzugsweise Geniposid oder Gentiopicrosid ist.

3. Verwendung nach Anspruch 1, wobei die Verbindung durch die folgende Formel (I-2) repräsentiert wird:

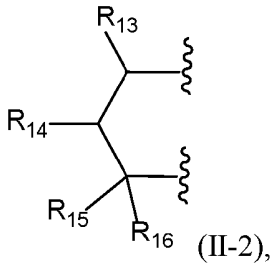


(I-2),

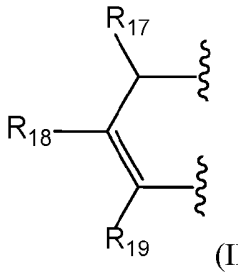
wobei:

- Y_1, Y_2 und Y_3 jeweils unabhängig ein Wasserstoff, -C(O)-Aryl oder -C(O)-(C_1-C_{12} aliphatische Gruppe) ist,
- R_{10} ein Wasserstoff, -C(O)OH oder -C(O)-O-(C_1-C_{12} aliphatische Gruppe) ist,
- R_{11} eine C_2-C_{12} aliphatische Gruppe, -CH_2-C(O)H, -CH_2-C(O)OH oder -CH_2-C(O)-O-(C_1-C_{12} aliphatische Gruppe) ist,
- R_{11}' ein Wasserstoff oder -OH ist,
- R_{12} -CH_2-C(O)H, eine C_2-C_{12} aliphatische Gruppe, -C(O)-CH_2-R_5 oder -CH(OH)-CH_2-R_5' ist, wobei R_5 und R_5' jeweils unabhängig ein Wasserstoffatom, eine C_1-C_{12} aliphatische Gruppe, -OH oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe) sind,
- R_{12}' ein Wasserstoff oder -OH ist,

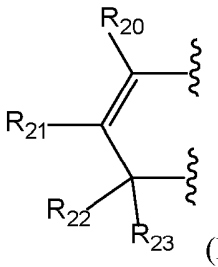
oder R_{11} und R_{12} zusammen eine der Ketten der Formel (II-2), (II-3), (II-4) oder (II-5) bilden:



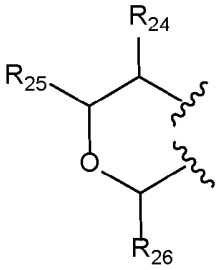
(II-2),



(II-3),

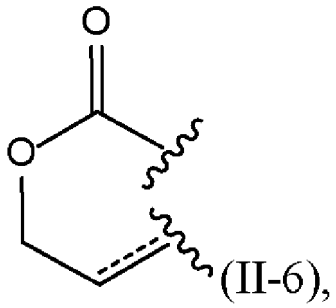


(II-4),



(II-5),

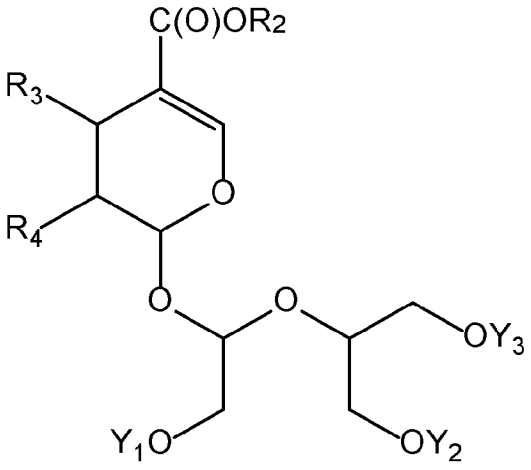
wobei jedes R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25} oder R_{26} unabhängig ein Wasserstoff, ein Halogen, -OH, -C(O)OH, -C(O)O-(C_1-C_{12} aliphatische Gruppe), -O-C(O)-(C_1-C_{12} aliphatische Gruppe), eine C_1-C_{12} aliphatische Gruppe, eine Hydroxy-(C_1-C_{12} aliphatische Gruppe) oder -CH_2-R_9' ist, wobei R_9' ein Wasserstoffatom, -OH, oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe) ist,
oder R_{14} und R_{15} zusammen eine -O-Gruppe bilden,
oder R_{10} und R_{11} zusammen eine Kette der Formel (II-6) bilden:



(II-6),

oder R_{12} und R_{12}' zusammen eine Gruppe der Formel R_{27}-CH= bilden, wobei R_{27} eine C_1-C_{12} aliphatische Gruppe, -C(O)OH, oder -C(O)O-(C_1-C_{12} aliphatische Gruppe) ist,
wobei die aliphatischen Gruppen jeweils unabhängig optional durch ein oder mehrere Hydroxy, Aryl, oder ein Glykosylderivat substituiert sind, wobei das Aryl optional durch ein oder mehrere Hydroxy oder (C_1-C_6) Alkoxy substituiert ist,
oder ein Salz davon.

4. Verwendung nach Anspruch 3, wobei die Verbindung durch die folgende Formel (I-1) repräsentiert wird:

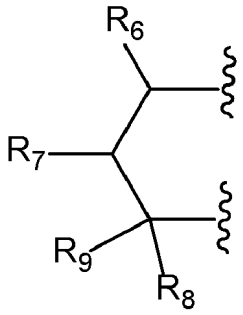


(I-1),

wobei:

- Y_1, Y_2 und Y_3 jeweils unabhängig ein Wasserstoff, -C(O)-Aryl, oder -C(O)-(C_1-C_{12} aliphatische Gruppe) ist,
- R_2 ein Wasserstoffatom oder eine (C_1-C_{12} aliphatischer Gruppe) ist,
- R_3 -CH_2-C(O)H oder -CH_2-CH_2-OH ist,
- R_4 -C(O)-CH_2-R_5, oder -CH(OH)-CH_2-R_5' ist, wobei R_5 und R_5' jeweils unabhängig ein Wasserstoffatom, eine C_1-C_{12} aliphatische Gruppe, -OH oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe) sind,

oder R_3 und R_4 zusammen die folgende Kette der Formel (II) bilden:



(II),

wobei R_6, R_7 und R_8 jeweils unabhängig ein Wasserstoffatom, -OH oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe) sind und R_9 ein Wasserstoffatom oder -CH_2-R_9' ist, wobei R_9'ein Wasserstoffatom, -OH oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe) ist,
oder ein Salz davon.

5. Verwendung nach Anspruch 4, wobei R_2 eine C_1-C_{12} aliphatische Gruppe ist, bevorzugt ein C_1-C_6 Alkyl.

6. Verwendung nach Anspruch 4 oder 5, wobei R_4 -C(O)-CH_2-R_5 oder -CH(OH)-CH_2-R_5' ist, wobei R_5 und R_5' jeweils unabhängig ein Wasserstoffatom, -OH oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe) sind, bevorzugt ein Wasserstoffatom, -OH oder -O-C(O)-(C_1-C_6 Alkyl).

7. Verwendung nach einem der Ansprüche 4 bis 6, wobei R_3 und R_4 zusammen die folgende Kette der Formel (II) bilden, wobei:

- R_6 Wasserstoff ist und/oder
- R_7 -OH oder -O-C(O)-(C_1-C_{12} aliphatische Gruppe), bevorzugt -OH oder -O-C(O)-(C_1-C_6 Alkyl) ist und/oder
- R_8 -OH ist und/oder
- R_9 ein Wasserstoffatom oder -CH_2-R_9' ist wobei R_9' ein Wasserstoffatom oder -O-C(O)-(C_1-C_6 Alkyl) ist.

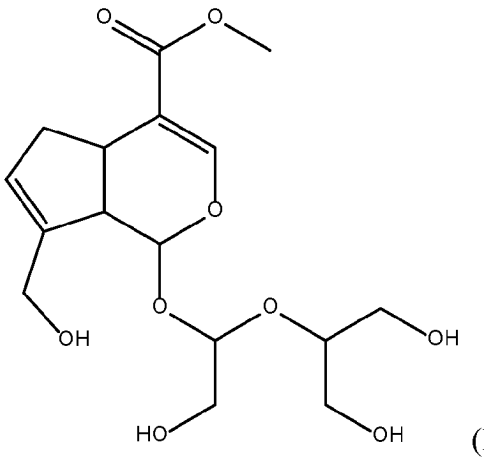
8. Verwendung nach einem der Ansprüche 1 bis 7, wobei jedes Y_1, Y_2 und Y_3 unabhängig ein Wasserstoff, -C(O)-Phenyl, oder -C(O)-(C_1-C_6 Alkyl), bevorzugt ein Wasserstoff oder -C(O)-CH_3, bevorzugter ein Wasserstoff ist.

9. Verwendung nach einem der Ansprüche 1 bis 8, zur Gerbung eines Fells oder einer Haut.

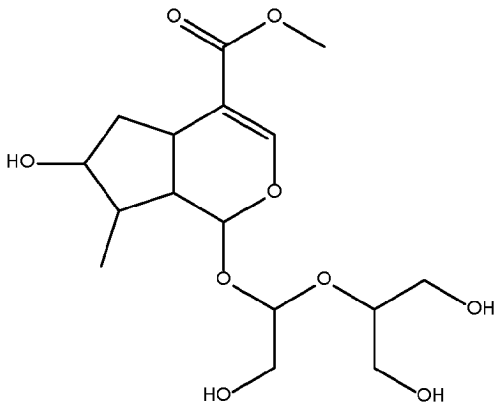
10. Verwendung nach einem der Ansprüche 1 bis 8 zur Gerbung eines Kollagenenthaltenden Materials.

11. Ein Verfahren zur Herstellung eines Leders oder eines Lederersatzstoffs, wobei das Verfahren die Verwendung nach einem der Ansprüche 1 bis 8 umfasst.

12. Eine nach einem der Ansprüche 1 bis 8 definierte Verbindung mit der Bedingung, dass die Verbindung nicht eine der folgenden Verbindungen ist:



(I-gen)



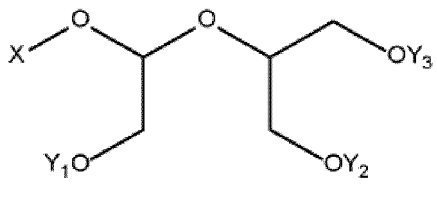
(I-log).

13. Ein Verfahren zur Quervernetzung von Kollagen in einem Material umfassend einen Schritt des in Kontaktbringen des Materials mit einer nach einem der Ansprüche 1 bis 8 und 12 definierten Verbindung.

14. Das Verfahren nach Anspruch 13, wobei das Material ein Fell oder eine Haut ist.

Revendications

1. Utilisation d'un composé de formule (I), dans un procédé de tannage :



(I),

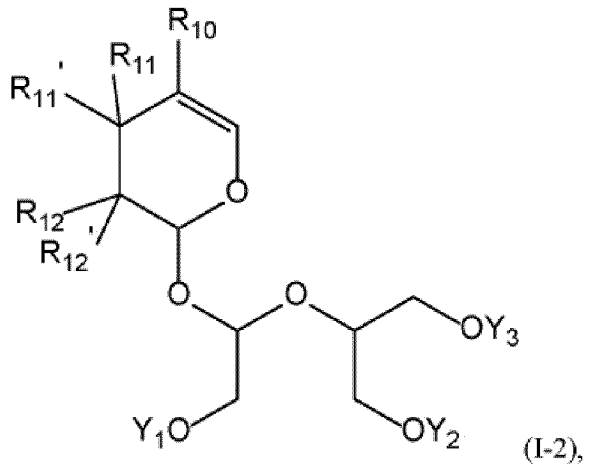
dans laquelle :

- X est une fraction d'un iridoïde, d'un séco-iridoïde ou d'un dérivé de celui-ci, et
- chacun de Y_1, Y_2 et Y_3 est indépendamment un hydrogène, -C(O)-aryle, ou - C(O)-(groupe aliphatique en C_1-C_{12}),

ou d'un sel de celui-ci.

2. Utilisation selon la revendication 1, dans laquelle X est une fraction d'aucubine, d'harpagide, de catalpol, d'ajugol, de géniposide, de loganine, d'acide loganique, d'antirrhinoside, de linarioside, de férétoside, d'acide géniposidique, de gardénoside, d'apodanthoside, d'acide désacétylaspérulosidique, de scandoside, d'ester méthylique de méthoxy-cinnamoyl scandoside, de déméthyloleuropéine, de ligustroside, d'acide ligustrosidique, de ligustaloside A, de ligustaloside B, de nuzhénide, de sécologanine, de sécoxyloganine, d'oleuropéine, d'hydroxyframoside A, d'hydroxyframoside B, de swéroside, de swertiamarine, de gentiopicroside, d'amarogentine, ou de morroniside, de préférence de géniposide ou de gentiopicroside.

3. Utilisation selon la revendication 1, dans laquelle ledit composé est représenté par la formule suivante (I-2) :

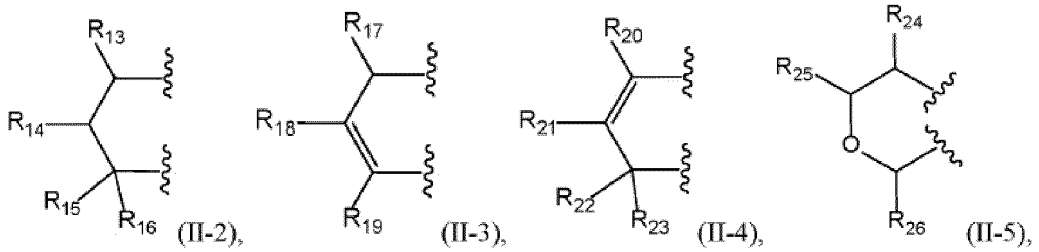


(I-2),

dans laquelle :

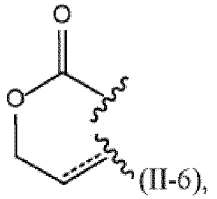
- chacun de Y_1, Y_2 et Y_3 est indépendamment un hydrogène, un -C(O)-aryle, ou un -C(O)-(groupe aliphatique en C_1-C_{12}),
- R_{10} est un hydrogène, -C(O)OH, ou -C(O)-O-(groupe aliphatique en C_1-C_{12}),
- R_{11} est un groupe aliphatique en C_2-C_{12}, -CH_2-C(O)H, -CH_2-C(O)OH, ou-CH_2-C(O)-O-(groupe aliphatique en C_1-C_{12}),
- R_{11}' est un hydrogène ou -OH,
- R_{12} est -CH_2-C(O)H, un groupe aliphatique en C_2-C_{12}, -C(O)-CH_2-R_5, ou-CH(OH)-CH_2-R_5' , où R_5 et R_5' sont chacun indépendamment un atome d'hydrogène, un groupe aliphatique en C_1-C_{12}, -OH, ou -O-C(O)-(groupe aliphatique en C_1-C_{12}),
- R_{12}' est un hydrogène ou -OH,

ou R_{11} et R_{12} forment conjointement l'une des chaînes de formules (II-2), (II-3), (II-4) ou (II-5) :



(II-2), (II-3), (II-4), (II-5),

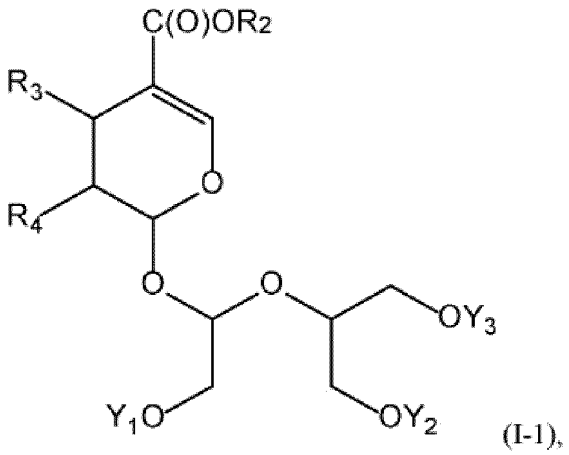
où chacun de R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, ou R_{26} est indépendamment un hydrogène, un halogène, -OH, -C(O)OH, -C(O)O-(groupe aliphatique en C_1-C_{12}), -O-C(O)-(groupe aliphatique en C_1-C_{12}), un groupe aliphatique en C_1-C_{12}, un hydroxy-(groupe aliphatique en C_1-C_{12}), ou -CH_2R_9', où R_9' est un atome d'hydrogène, -OH, ou -O-C(O)-(groupe aliphatique en C_1-C_{12}),
ou R_{14} et R_{15} forment conjointement un groupe -O-,
ou R_{10} et R_{11} forment conjointement une chaîne de formule (II-6) :



(II-6),

ou R_{12} et R_{12}' forment conjointement un groupe de formule R_{27}-CH=, où R_{27} est un groupe aliphatique en C_1-C_{12}, -C(O)OH, ou -C(O)O-(groupe aliphatique en C_1-C_{12}),
lesdits groupes aliphatiques étant chacun indépendamment éventuellement substitués par un ou plusieurs hydroxy, aryle ou un dérivé de glycosyle, ledit aryle étant éventuellement substitué par un ou plusieurs hydroxy ou alcoxy (en C_1-C_6),
ou un sel de celui-ci.

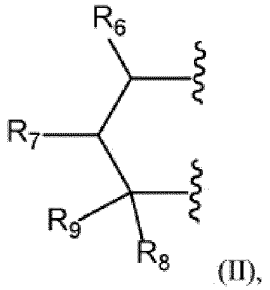
4. Utilisation selon la revendication 3, dans laquelle ledit composé est représenté par la formule suivante (I-1) :



(I-1),

dans laquelle :

- chacun de Y_1, Y_2 et Y_3 est indépendamment un hydrogène, -C(O)-aryle, ou - C(O)-(groupe aliphatique en C_1-C_{12}),
- R_2 est un atome d'hydrogène ou un groupe aliphatique (en C_1-C_{12}),
- R_3 est -CH_2-C(O)H ou -CH_2-CH_2-OH,
- R_4 est -C(O)-CH_2-R_5 ou -CH(OH)-CH_2-R_5', où R_5 et R_5' sont chacun indépendamment un atome d'hydrogène, un groupe aliphatique en C_1-C_{12}, -OH, ou -OC(O)-(groupe aliphatique en C_1-C_{12}),
ou R_3 et R_4 forment conjointement la chaîne suivante de formule (II) :



(II),

dans laquelle R_6, R_7, et R_8 sont chacun indépendamment un atome d'hydrogène,-OH, ou -O-C(O)-(groupe aliphatique en C_1-C_{12}), et R_9 est un atome d'hydrogène ou-CH_2R_9', où R_9' est un atome d'hydrogène, -OH, ou -O-C(O)-(groupe aliphatique en C_1-C_{12}),
ou un sel de celui-ci.

5. Utilisation selon la revendication 4, dans laquelle R_2 est un groupe aliphatique en C_1-C_{12}, de préférence un alkyle en C_1-C_6.

6. Utilisation selon la revendication 4 ou 5, dans laquelle R_4 est -C(O)-CH_2-R_5 ou -CH(OH)-CH_2-R_5', où R_5 et R_5' sont chacun indépendamment un atome d'hydrogène, -OH, ou -O-C(O)-(groupe aliphatique en C_1-C_{12}), de préférence un atome d'hydrogène, -OH, ou -O-C(O)-(alkyle en C_1-C_6).

7. Utilisation selon l'une des revendications 4 à 6, dans laquelle R_3 et R_4 forment conjointement la chaîne suivante de formule (II) dans laquelle :

- R_6 est hydrogène ; et/ou
- R_7 est -OH ou -O-C(O)-(groupe aliphatique en C_1-C_{12}), de préférence -OH ou -O-C(O)-(alkyle en C_1-C_6) ; et/ou
- R_8 est -OH ; et/ou
- R_9 est un atome d'hydrogène ou -CH_2R_9', R_9' étant un atome d'hydrogène ou-O-C(O)-(alkyle en C_1-C_6).

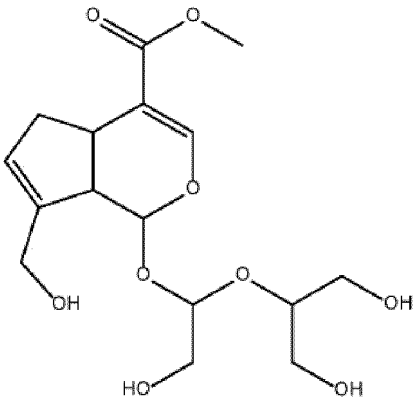
8. Utilisation selon l'une des revendications 1 à 7, dans laquelle chacun de Y_1, Y_2 et Y_3 est indépendamment un hydrogène, -C(O)-phényle, ou -C(O)-(alkyle en C_1-C_6), de préférence un hydrogène ou -C(O)-CH_3, plus préférentiellement un hydrogène.

9. Utilisation selon l'une quelconque des revendications 1 à 8, pour le tannage d'une fourrure ou d'une peau.

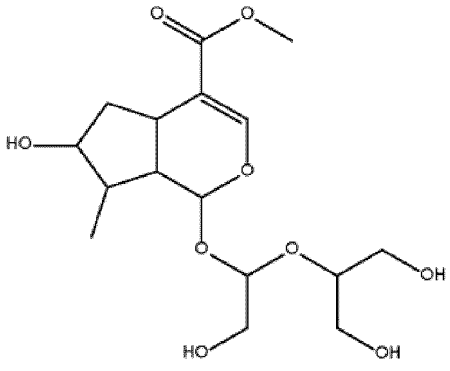
10. Utilisation selon l'une quelconque des revendications 1 à 8, pour le tannage d'une matière contenant du collagène.

11. Méthode pour la fabrication d'un cuir ou d'un substitut de cuir, la méthode comprenant l'utilisation selon l'une quelconque des revendications 1 à 8.

12. Composé tel que défini dans l'une quelconque des revendications 1 à 8, à condition que ledit composé ne soit pas l'un des composés suivants :



(I-gen)



(I-log).

13. Procédé de réticulation du collagène dans une matière comprenant une étape de mise en contact de ladite matière avec un composé tel que défini dans l'une quelconque des revendications 1 à 8 et 12.

14. Procédé selon la revendication 13, dans lequel ladite matière est une fourrure ou une peau.

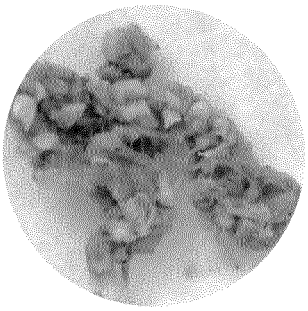


Table 1, entry 1

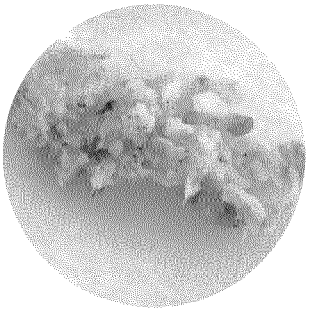


Table 2, entry 1

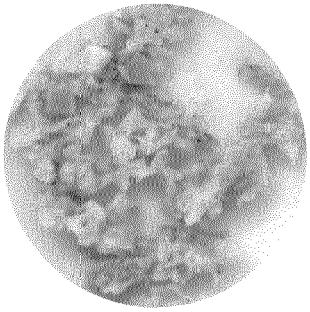


Table 2, entry 2

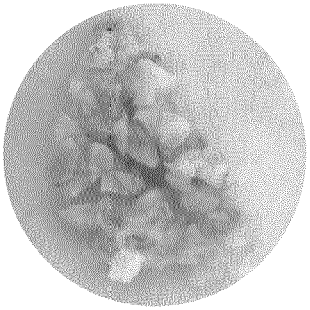


Table 2, entry 3

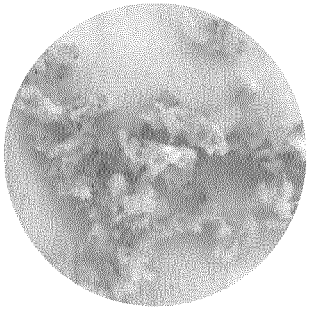


Table 2, entry 4

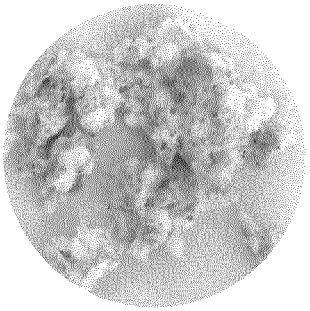


Table 2, entry 5

Figure 1

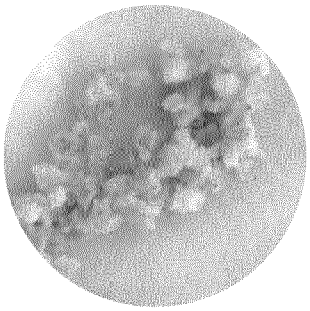


Table 3, entry 1

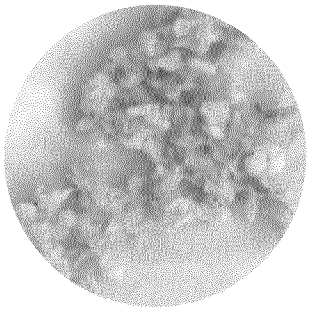


Table 3, entry 2

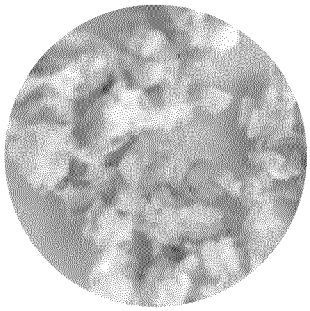


Table 3, entry 3

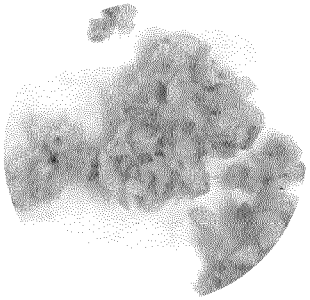


Table 3, entry 4

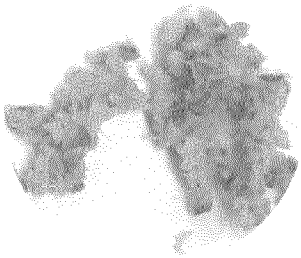


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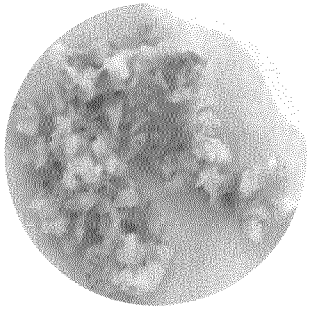


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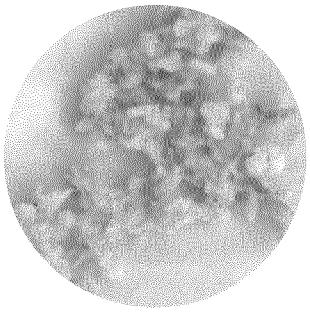


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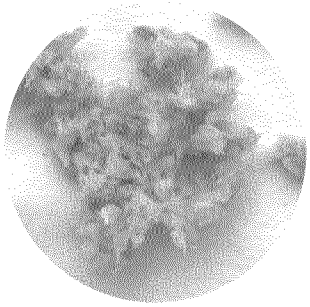


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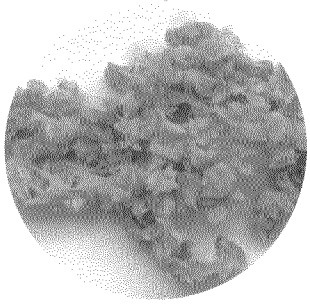


Table 4, entry 3

Figure 2

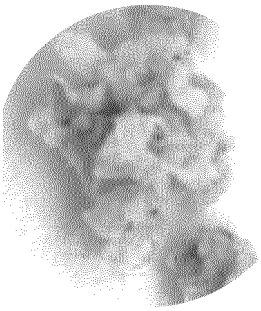


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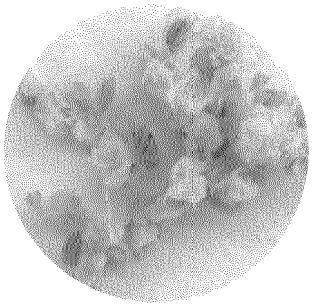


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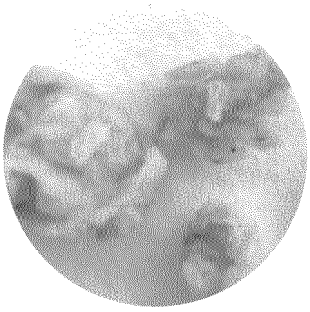


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Figure 3

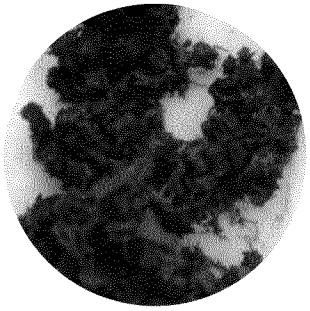


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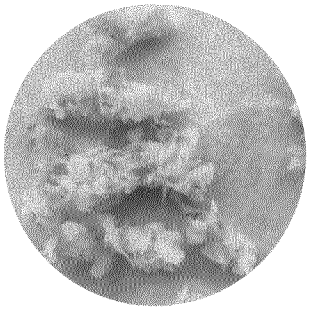


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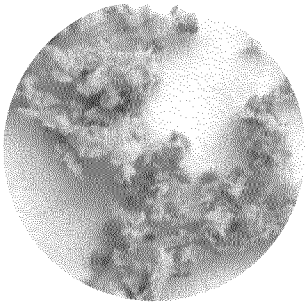


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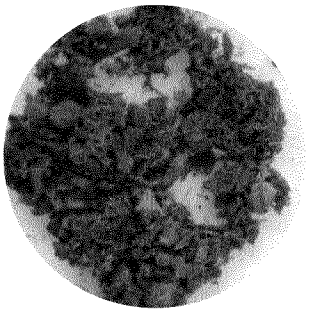


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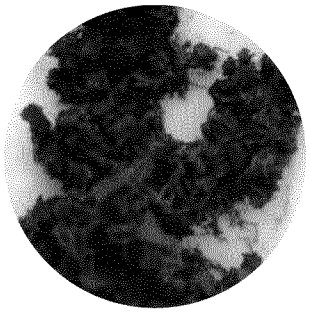


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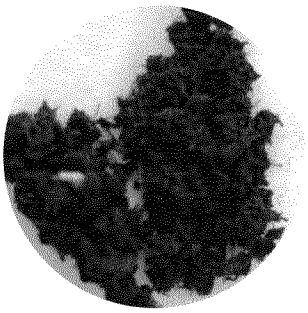


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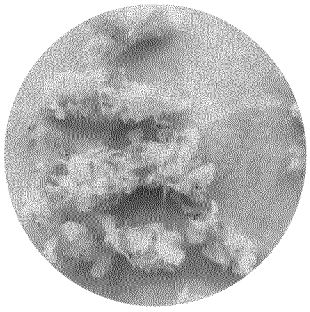


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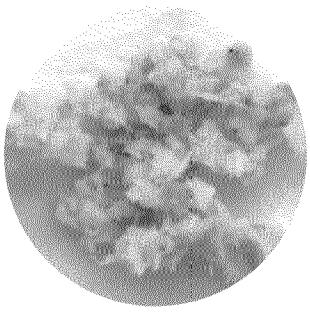


Table 8, entry 2

Figure 4

REFERENCES CITED IN THE DESCRIPTION

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