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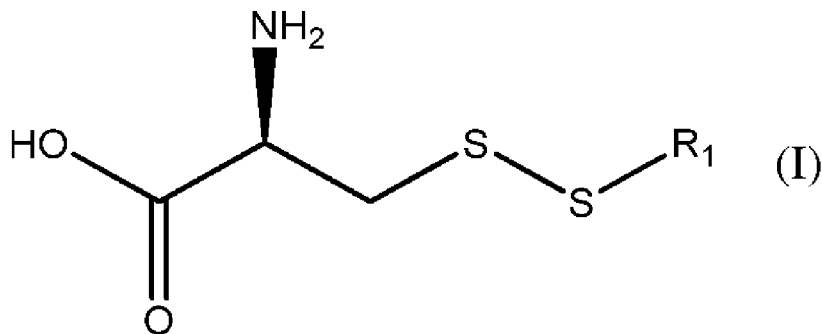
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(54) Title: TASTE MODIFYING COMPOUND



(57) Abstract: The invention provides the use as a flavor precursor of a compound according to formula (I) wherein R₁ is a C₁ to C₅ alkyl or alkenyl group for the generation of certain highly valued onion notes.

TASTE MODIFYING COMPOUND

Technical field

The present invention relates to the field of taste. More particularly, it relates to
5 flavor precursors capable of retaining flavors upon storage and releasing them at a later stage.

The present invention also concerns compositions or articles containing at least one of the aforementioned compounds.

10 Background and Prior art

Flavors are used to provide an olfactive and gustatory experience when consuming food. However, many foods require one or more processing steps which involve the use of heat to fulfil various needs, e.g. cooking, sterilization or pasteurization, generation of reaction flavors and so on. This can have adverse consequences upon volatile flavors
15 which can be lost or even destroyed by such heating processes. For this reason, it is known to encapsulate flavors by such methods as extrusion, spray-drying, spray-chilling, coacervation and the like. Such methods can be effective but they can retard undesirably or interfere with the flavor itself, they add complexity to the flavor system and they can even be visible to the naked eye which may in certain circumstances be undesirable.
20 Thus, it would be desirable to provide a flavor that, even if volatile, can survive storage and be released under certain conditions at a desired stage.

The principle of using flavor precursors is known. For instance, WO-A1-2008/011744 describes precursors of these relate to mono or diglyceride-based lactone flavors.

25 Onions have been used in foodstuffs and cooking since time immemorial and onion flavor is highly desirable in many applications, such as snack foods. To date, the most usual onion flavor has been onion itself, usually in dried powder and flake form. While this is generally satisfactory, the onions from which the powders and flakes are made can vary in quality and availability, making the achievement of a satisfactory and
30 consistent onion flavor sometimes difficult.

The provision of an onion flavor is described in EP-A-2165612 (Givaudan) where there is provided a flavoring composition comprising a compound selected from S-allyl cysteine and S-1-propenyl cysteine. However, these compounds are limited in that they

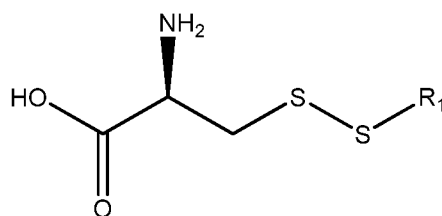
are transformed primarily into 1-sulfanyl-2-propene and 1-sulfanyl-1-propene, which are not fully representative of a rounded onion or garlic flavor insofar as only minute amounts of other important compounds, such as disulfides and polysulfides, may be formed. It would be desirable to address this issue.

5 The cysteine propylsulphide conjugate is described in the publication “Cysteine and Glutathione Mixed-Disulfide Conjugates of Thiosulfinates: Chemical Synthesis and Biological Activities”, Guodong Zhang, Bin Li, Chen-Hsien Lee, Kirk Parkin, Journal of Agriculture and Food Chemistry 2010, 58, 1564–1571. However, this article refers only to the capacity of various conjugates to induce quinine reductase (QR, a representative
10 phase II enzyme) in murine hepatoma cells (Hepa 1c1c7) and to inhibit nitric oxide (NO) production in lipopolysaccharide (LPS)-stimulated macrophage cells (RAW 264.7), indicating they have potential cancer preventive and anti-inflammatory activities. Nowhere in this document is there any suggestion that one class of the compounds described therein is suitable for use as flavor precursors.

15 Thus, to the best of our knowledge no mention or suggestion of any of the compounds of formula (I) below for use as flavor precursors below is made in the prior art.

Summary of the invention

20 We have now surprisingly discovered that a compound having the formula

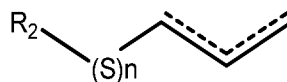


Formula (I)

25 wherein R₁ is a C₁ to C₅ alkyl or alkenyl group provides a new flavor precursor for the generation of certain highly valued onion notes.

Accordingly, the present invention provides the use as a flavor precursor of a compound according to formula (I).

30 The invention further provide the use of a compound according to formula (I) as a flavor precursor to release a flavor composition comprising two or more different compounds having the structure according to formula (II)



Formula (II)

- 5 wherein R_2 represents H or a C_1 to C_3 alkyl or alkenyl chain, n represents an integer from 1 to 4 and each dotted line independently denotes that a single or double bond is present.

In a preferred aspect of the invention, there is provided a composition comprising the flavor precursor according to formula (I) in combination with at least one ingredient selected from the group consisting of a flavor carrier, flavor base and optionally at least
 10 one flavor adjuvant, the combination providing a flavored article.

In another aspect there is provided a flavor precursor according to formula (I) as part of or incorporated into a foodstuff.

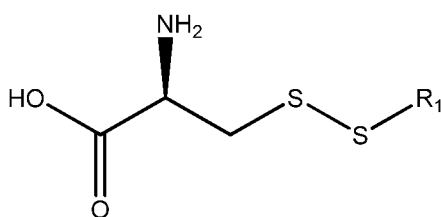
In still a further aspect there is provided a method to enhance, improve or modify the flavor or taste of a flavoring composition or a flavored product, which comprises
 15 adding thereto a flavor precursor according to formula (I).

In the context of the present invention, the flavor precursor according to formula (I) includes all isomers and salts thereof as well as any mixture of the isomers and/or salts. Thus, although the R-enantiomer is shown above, the flavor precursor may comprise the S-enantiomer, the R-enantiomer or a mixture thereof. Nevertheless, the
 20 R-enantiomer is preferred.

Detailed Description of the Invention

The flavor precursor, as herein defined, is a compound according to the following
 formula

25

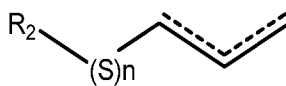


Formula (I)

wherein R_1 is a C_1 to C_5 alkyl or alkenyl group.

In a preferred aspect, R_1 is a C_1 to C_3 alkyl or alkenyl group. More preferably R_1 is a C_2 to C_4 alkyl or alkenyl group. Even more preferably R_1 is a C_3 alkyl or alkenyl group. Most preferably R_1 is a propenyl moiety.

The flavor precursor is preferably used for releasing at least two compounds
 5 having the structure according to formula (II)



Formula (II)

10 wherein R_2 represents H or a C_1 to C_3 alkyl or alkenyl chain, n represents an integer from 1 to 4 and each dotted line independently denotes that a single or double bond is present and further wherein for the first compound, n is equal to 2 and for the second compound, n is not equal to 2.

It is particularly preferred that the flavor precursor releases a mixture of
 15 compounds comprising a disulfide and a trisulfide according to formula (II).

Most preferably there is a large excess of the disulfide compound generated since it is this molecule that provides a key desirable onion flavor. This is achieved by the use of the precursor according to the invention. Indeed, it is found that the amount of disulfide generated is typically greater than 65% by weight based on the total weight of
 20 flavors generated by the precursors, and may even be greater than 70% by weight.

Flavor Precursor Mixture

The flavor precursor is preferably used in a food product requiring an onion or alliaceous character. For instance, savory foods, where a garlic or onion-like note is
 25 desired, can benefit from the presence of these flavor precursors according to the present invention.

A flavor composition according to the invention is a composition that comprises a flavor precursor according to formula (I) and an additional different flavor ("flavor co-ingredient") and/or a flavor adjuvant. Flavors for use as the flavor co-ingredient are
 30 described in numerous literature references such as S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, New Jersey, USA, or in other works of a similar nature, as well as in the abundant patent literature in the field of flavor and the skilled flavorist is

readily capable of selecting suitable flavor co-ingredients based on his general knowledge and according to the intended application or desired organoleptic effect.

Flavor adjuvants are well known and may be selected from, for example, without limitation, solvents, binders, diluents, disintegrating agents, lubricants, coloring agents, 5 preservatives, antioxidants, emulsifiers, stabilisers, flavor-enhancers, sweetening agents, anti-caking agents, enzymes, enzyme-containing preparations and the like. Examples of carriers or diluents for flavor or fragrance compounds can be found in, for instance, "Perfume and Flavor Chemicals", S. Arctander, Ed., Vol. I & II, "Perfume and Flavor Materials of Natural Origin", S. Arctander, 1960; in "Flavorings", E. Ziegler and 10 H. Ziegler (ed), Wiley-VCH Weinheim, 1998, and "CTFA Cosmetic Ingredient Handbook".

In a preferred embodiment, a flavor composition comprises the flavor precursor according to formula (I) and an enzyme.

The flavor composition may be added in any suitable form, for example as a 15 liquid, as a paste, or in encapsulated form bound to or coated onto carriers/particles or as a powder.

Foodstuffs

In the context of the present invention "foodstuffs" denotes any composition 20 consumed for nutrition or pleasure. Typical examples include, but are not limited to soups, broths, bouillons, stews, gravies, meat and vegetable extracts, powdered soups, instant noodles, dried pesto mixes, dried savory dishes, stable in-dough flavoring for noodles, frozen foods and snack foods.

Since the present invention relates to a flavor precursor that is particularly suitable 25 for releasing an onion flavor, especially desirable foodstuffs are snack foods, such as crisps and chips, based on potatoes, corn (maize), rice and tapioca.

The flavor precursor may be encapsulated. Suitable encapsulation systems for the flavor precursors of the present invention are described below.

The proportions in which the compounds according to the invention can be 30 incorporated into the various aforementioned articles or products vary within a wide range of values. These values are dependent on the nature of the article to be flavored and on the desired organoleptic effect, as well as the nature of the co-ingredients in a given

base, when the compounds according to the invention are mixed with flavoring co-ingredients, solvents or additives commonly used in the art.

In the case of flavored products, the minimum concentration of flavor precursor (I) is preferably at least 0.1 ppm, more preferably 0.2 ppm, even more preferably 0.5 ppm and most preferably 1 ppm. The maximum concentration is preferably 100 ppm, more preferably 80 ppm, even more preferably 70 ppm and most preferably 50 ppm.

Examples

The invention will now be described in further detail by way of the following examples, wherein the abbreviations have the usual meaning in the art, the NMR spectral data were recorded in CDCl₃, with a 400MHz machine for ¹³C, the chemical displacements, δ , are indicated in ppm with respect to TMS as standard, and the coupling constants, *J*, are expressed in Hz.

Example 1

Synthesis of S-propyl-L-cysteine disulfide

3-[(Methoxycarbonyl)dithio]-L-alanine (0.5 g, 2.0 mmole) in anhydrous methanol (10 mL) was added to 1-propane thiol (2 mL, 22 mmole), triethylamine (0.7 mL, 5 mmole) and ethanol. The pH was maintained between 8 and 9 by adding triethylamine (3 x 0.3 mL), then the reaction was stirred over night. The resulting mixture was diluted with water 100 mL and the organic compounds were extracted with pentane. The water phase was loaded on a SiO₂-RP18 column (internal diameter 4.5 cm, level of dry phase 10 cm). The column was rinsed with water (400 mL), then water with 10% EtOH (200 mL) and the product was eluted with water containing 30% EtOH (500 mL). The product was then lyophilized to provide powdered S-propyl-L-cysteine disulfide (750 mg, yield 69%).

HPLC-TOF High-Resolution MS: C₆H₁₄NO₂S₂, calculated mass 195.03877, measured 195.03709 (difference 8.6 ppm).

HPLC-ESI⁺ (BEH-C18, 150): 4.61 min. (MW+H) 196, for SRM fragments used: 107 (100%).

¹³C NMR : δ 15.2 (q), 24.6 (t), 39.6 (t), 42.7 (t), 54.6 (d), 173.4 (s) (5).

Example 2

Preparation of *S*-allyl-L-cysteine disulfide

3-[(Methoxycarbonyl)dithio]-L-alanine (4.2 g, 16.9 mmole) in anhydrous methanol
5 (30 mL) was added to 2-propene thiol (5.37 g, 74 mmole), triethylamine (2.61 g, 25.8 mmole) and ethanol 30 mL. The pH was maintained between 8 and 9 by adding triethylamine (3 x 0.3 mL), then the reaction was stirred over night. The resulting mixture was diluted with water (100 mL) and the organic compounds were extracted with pentane. The water phase was loaded on a SiO₂-RP18 column (internal diameter 4.5 cm,
10 level of dry phase 10 cm). The column was rinsed with water (400 mL), then the product was eluted with water containing 10, 20, 30 and 40% EtOH (200 mL). The compound **8** was in fractions eluted with 30% aqueous EtOH. The product was then lyophilized to provide *S*-allyl-L-cysteine disulfide (1.6 g, yield 49%).

HPLC-TOF High-Resolution MS: C₆H₁₂NO₂S₂, calculated mass 193.0228, measured
15 193.02312 (difference 1.6 ppm).

HPLC-ESI⁺ (BEH-C18, 150): 2.70 min. (M+1) 194, for SRM fragments used: 152 (100%), 105 (30%).

¹³C NMR : δ 39.7 (t), 43.5 (t), 54.6 (d), 122.2 (t), 136.2 (d), 173.6 (s). (5)

Example 3

Preparation of 3 *S*-(1-propenyl)-L-cysteine disulfide

(*E/Z*)-1-Propenethiol was obtained after reduction of bis[(*E/Z*)-1-propenyl] disulfide (0.9 g, 6 mmole) (**16**) with LiAlH₄ (0.24 g, 6 mmole) in Et₂O (20 mL) over night at room
25 temperature. Salts and excess LiAlH₄ were removed after careful addition of ice water and HCl 2 M. The organic phase was separated and dried on Na₂SO₄. The volume of Et₂O was reduced to 5 mL and the solution was added to 3-[(methoxycarbonyl)dithio]-L-alanine (5.5 mmole) in anhydrous methanol (10 mL). Triethylamine was added (0.7 mL, 5 mmole) until the pH was 3-4. After one hour an additional 0.2 mL of triethyl amine was
30 added until the pH was 6-7, then the reaction was stirred over night. The resulting mixture was diluted with water (100 mL) and the organic compounds were extracted with pentane. The water phase was loaded on a SiO₂-RP18 column (internal diameter 4.5 cm, level of dry phase 10 cm). The column was rinsed with water (400 mL), then water with 10% EtOH (200 mL), water with 20% EtOH (200 mL) and the product was eluted with

aqueous EtOH 30% (400 mL). The product was lyophilization to obtain 400 mg of a white powder which was further purified by chromatography under the same conditions and only the purest fraction, containing **7**, was retained (60 mg, yield 9%).

HPLC-TOF High-Resolution MS: $C_6H_{12}NO_2S_2$, calculated mass 193.02101, measured 193.02312 (difference 10.9 ppm).

HPLC-ESI⁺ (BEH-C18, 150): 4.48 min. (M+1) 194, for SRM fragments used: 105 (100%), 131 (40%). No separation of (E/Z) isomers.

7-(Z): ¹H NMR: δ 6.19 (dq, J = 9.1, 1.6, 1H, H-4); 5.96 (dq, J = 9.1, 6.9, 1H, H-5); 4.26-4.21 (m, 1H, H-2); 3.34 (dd, J = 15.1, 4.0, 1H, H-3); 3.16 (dd, J = 15.1, 8.2, 1H, H-3'); 1.77 (dd, J = 6.9, 1.6, 3H, H-6). ¹³C NMR: δ 174.7 (s), 134.5 (d), 129.0 (d), 55.4 (d), 39.6 (t), 16.8 (q);

7-(E) ¹H NMR: δ 6.17-6.14 (m, 2H, H-4 and H-5); 4.26-4.21 (m, 1H, H-2); 3.38 (dd, J = 15.1, 4.1, 1H, H-3); 3.17 (dd, J = 15.1, 7.8, 1H, H-3'); 1.79 (m, 3H, H-6); ¹³C NMR: δ 174.6 (s), 137.8 (d), 125.1 (d), 55.5 (d), 40.6 (t), 20.4 (q).

Example 4

Onion Soup Preparations

Two flavoring compositions, (A) and (B), for onion soup, are prepared by admixing the following ingredients:

Table 1

	Composition (A)	Composition (B)
<u>Ingredient</u>	<u>Parts by weight</u>	<u>Parts by weight</u>
Dimethyl sulfide	50	50
Diallyl disulfide	5	5
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	200	200
2-Methyl-3-thiol-furane	2	2
Decenal	10	10
Dipropyldisulfide	20	20
Decadienal	5	5
1,2,3-Propanetriyl triacetate	708	658
Flavor precursor*	-----	500
Total	1000	1000

* prepared as in example 1

To a portion of a standard unflavored canned onion soup are added 20 ppm, relative to the weight of the soup, of the flavoring composition (A).

To the other portion of the above unflavored canned onion soup are added 20 ppm,
5 relative to the weight of the soup, of the flavoring composition (B).

There are thus obtained two flavored canned onion soups, one containing flavor compound from example 1 and the other not containing it.

The soup containing composition (A) has an aggressive, roasted onion and caramelized character.

10 The soup containing composition (B) has a flavor with a rounded alliaceous, oniony character.

Example 5

Garlic Flavor Preparations

15 A typical flavor having a garlic roast type flavor character is prepared by admixing the following ingredients in the amounts indicated:

Table 2

20

Ingredients	Parts by weight
Acetylpyrazine at 1.00%*	30.000
Ethyl acrylate at 10.00%*	10.000
Heptanal at 10.00%*	15.000
Benzylmercaptan at 10.00%*	15.000
Caryophyllene at 10.00%*	10.000
Cis-3-hexenol formate at 1.00%*	20.000
2,3,5-Trimethylpyrazine at 10.00%*	70.000
2-Ethyl-3-methylpyrazine at 10.00%*	60.000
Thiol at 10.00%*	40.000
Decanoic acid redist.	5.000
Garlic essential oil	20.000
Isovaleric aldehyde	5.000

3-Propylidene-1-benzo(C)furanone	10.000
Benzothiazole	20.000
Furaneol ^{® 1)}	25.000
Methylfurfural	40.000
Methylnussol at 10.00%**	10.000
Mustard essential oil	30.000
(E)-2-hexenal	5.000
Diallyl sulfide	350.000
Dipropyl disulfide	50.000
5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone at 1.00%*	5.000
Nussol extra	10.000
Propylmercaptan at 10.00%*	100.000
Sulfurobase ¹⁾	30.000
Dimethyl trisulfide at 10.00%*	15.000
Total	1000.000

* In triacetine

** In ethyl citrate

1) Origin: Firmenich SA, Geneva, Switzerland

5

To this flavor composition there is added the flavor precursor as defined in example 3 in an amount sufficient to provide a final concentration of 1 ppm of this extract in a tasting saline solution (salt 0.5%, MSG 0.05% w/w) where the flavor is used in an amount of 0.001 ppm. The flavor precursor of the invention increases the rounded alliaceous character of the flavor.

10

Example 6

Beef bouillon preparation

15 A beef bouillon has the following ingredients in the amounts shown. The bouillon is prepared by thoroughly mixing the ingredients.

Table 3

Ingredient	% by weight
Onion powder (1)	1.0
Table Salt	25.0
Caramel Color (2)	1.0
Light Yeast (3)	5.0
Ground white pepper	0.05
Sugar	3.0
Beaded palm oil	12.0
Parsley	0.10
Yeast Enhancer (4)	2.5
Butter Oil	5.0
Maltodextrin (5)	44.35

(1) ex Firmenich, ref. 967746

5 (2) ex Firmenich, ref. 927409

(3) ex Firmenich, ref. 946686

(4) ex Firmenich, ref. 992444

(5) ex Firmenich, ref. 909251

- 10 20 g of the bouillon is then added to 1 litre of hot water and stirring until dissolved. Next 20 ppm of the flavor precursor as defined in example 3 is added to provide a solution having an enhanced onion note.

Example 7

15 Instant vegetable cream soup

An instant vegetable cream soup has the following ingredients in the amounts shown. The soup is prepared by thoroughly mixing the ingredients.

20 Table 4

Ingredient	% by weight
Creaming agent (1)	22.0
Table Salt	7.5
Yeast extract (2)	3.0

Skimmed milk powder	12.0
Onion powder	2.7
Modified starch (3)	33.0
Beaded palm oil (4)	1.6
Monosodium glutamate	1.5
Garlic powder (5)	0.15
Tomato powder (6)	2.4
Carrot powder (7)	1.2
Leek powder (8)	2.0
Red bell pepper (9)	0.45
Rubbed parsley	0.25
Maltodextrin	10.25

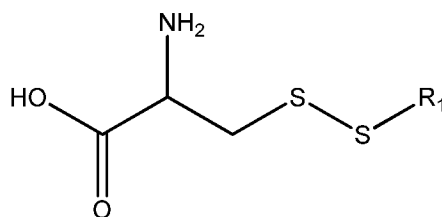
- (1) ref. 936110
- (2) ref. 946686
- (3) VA70T, ex Prejel.
- 5 (4) ref. 948082
- (5) ref. 905113
- (6) ref. 988136
- (7) ref. 920511
- (8) ref. 974504
- 10 (9) ref. 974548
- (10) ref. 909251

The soup is prepared by mixing the ingredients thoroughly, and 100g of the mixture is added to 1 liter of hot water and stirred until dissolved. The soup is then divided into

15 2 portions, to one of which is added 20ppm of the flavor precursor prepared in example 3. The soup containing the compound of example 1 has a more rounded onion note.

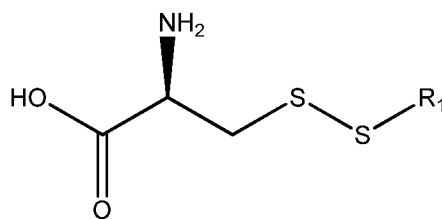
Claims

1. Use as a flavor precursor of a compound according to formula (I)



Formula (I)

2. Use according to claim 1 wherein the compound has the structure



Formula (I')

3. Use according to any one of the preceding claims wherein R_1 is a C_1 to C_3 alkyl or alkenyl group.

4. Use according to any one of the preceding claims wherein R_1 is a C_2 to C_4 alkyl or alkenyl group.

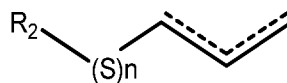
5. Use according to any one of the preceding claims wherein R_1 is a C_3 alkyl or alkenyl group

6. Use according to any one of the preceding claims wherein R_1 is a propenyl group.

7. Use according to any one of the preceding claims wherein the flavor precursor releases an onion or alliaceous flavor.

8. Use of the compound according to claim 1 or claim 2 as a flavor precursor to release a flavor composition comprising at least a first and a second compound having the structure according to formula (II)

5



Formula (II)

wherein R_2 represents H or a C_1 to C_3 alkyl or alkenyl chain, n represents an integer from 1 to 4, each dotted line independently denotes that a single or double bond is present and further wherein for the first compound, n is equal to 2 and for the second compound, n is not equal to 2.

9. Use according to claim 8 wherein the two or more different compounds comprise a disulfide and a trisulfide.

10. Use according to claim 8 wherein the content of disulfide generated is greater than 65% by weight based on the total weight of flavors generated by the flavor precursor(s).

20

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/059142

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/227
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23L

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

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

EPO-Internal, WPI Data, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 197709 Thomson Scientific, London, GB; AN 1977-15546Y XP002430730, & JP 52 007468 A (SHIONO KORYO KK) 20 January 1977 (1977-01-20) abstract	1-10
A	----- EP 2 165 612 A1 (GIVAUDAN SA [CH]) 24 March 2010 (2010-03-24) cited in the application abstract ----- -/-	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/059142

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