

Bis(acetylthio)methane as a fragrance ingredient, fragrance, and perfumed products comprising it.

This application claims the benefit of European Patent Application EP23383224 filed 28
5 November 2023.

Technical Field

10 The invention relates to the field of fragrance ingredients, as well as to perfuming compositions and perfumed products containing them.

Background Art

15 At present, the use of fragrances is widespread in a large number of commonly used consumer products, such as fine fragrances, personal care products, home care products, air freshener products, and the like, which causes the perfume industry to increasingly need new fragrance ingredients that offer new olfactory benefits.

20 A wide variety of odoriferous materials are known for use in perfumery, including materials such as alkenes, alcohols, aldehydes, ketones, esters, ethers, nitriles, amines, oximes, acetals, ketals, thiols, thioketones, imines, etc.

US5871721 discloses S,S-ethylidene dithioacetate as an active perfuming ingredient and
25 also as a flavoring agent for various products such as foodstuffs, beverages, chewing gum, toothpastes, or pharmaceutical preparations. According to this document it has a natural sulfurous odor with an attractive herbaceous quality and leathery edge. The compound is described as a multi-odor product which also develops hints of garlic, onion, galbanum, or bergamot notes, reminiscent of the bergamot leaf absolute, having a
30 powerful odor that can be used in very dilute concentrations and also having a lasting odor.

In the fragrance industry there is a constant demand for new fragrance ingredients capable of creating interesting olfactory sensations and of expanding the possibilities of perfume creation with their new olfactory properties. In addition, fragrance ingredients that
35 fulfill this primary function should preferably contribute to olfactory properties such as high intensity, longevity, high substantivity, malodor-eliminating effect or aroma-enhancing properties, when combined with other fragrance ingredients, so that novel sensory effects can be achieved from the fragrance compositions.

Bis(acetylthio) methane is known from the production of polymers, and it has also been used in the field of flavors. EP1090557A1 discloses a mixture of at least 2 sulfur molecules to get meaty, savory flavors. The first molecule is a 2-methyl-3-furyl-thio moiety. The second one is one with the structure U-CH₂-S-T, which includes, among others, bis(acetylthio)methane. As is seen in Example 10 of this document, in a flavour formula they are present at a concentration of 1600 ppm each. This is much higher than the amounts used in fragrance formulas. The role of the combination of the two groups of sulfur compounds in the final food leads to a food stuff with powerful flavor reminiscent of beef broth. It seems that the role of bis(acetylthio)methane in this combination is to improve the meat, beef, savory effect of a 2-methyl-3-furyl-thio moiety. However, a skilled person wishing to get a powerful fragrance that could be used in very low concentrations would not have looked at a document describing savory flavorings because the described sensory effect is very far from those desired in fragrances. Besides, many flavor molecules are not interesting for fragrances at all.

Finally, one phenomenon that seriously disrupts attempts to correlate odor properties with molecular structure is that a given structural modification can induce a dramatic change in odor properties in one situation whilst having little or no effect in another. Thus, despite great deal of research on structure–odor relationships to date, prediction of the odor of a novel molecule remains a statistical exercise and models only provide a probability of the character, threshold, and intensity. Surprises are still commonplace, and serendipity continues to be an important factor in the discovery of novel fragrant molecules (see C.S. Sell in “On the Unpredictability of Odor”, *Angew. Chem. Int- Ed.* 2006, vol. 45, pp.6254-6261).

Summary of Invention

Inventors have found that bis(acetylthio) methane (BATM) has an unexpected perfumery role (contributing with descriptors such as marijuana and green smell) and strong intensity at very low concentration, that makes it effective as a fragrance ingredient. The compound alone presents descriptors such as marijuana, green, mocha, fresh, yeasts, fermentation, spicy, and leather. The value of this compound lies in that it can be used at very low dosage having a very intense odor fragrance.

As it is illustrated in the Examples, it has a very low odor threshold and, most importantly, still has a sensory effect when applied to fragrances, i.e., this means that fragrance benefits are perceived when the compound is incorporated in a fragrance at very low dosage. Furthermore, its use at very low dosage is advantageous because of the less volume and because the product can be used as a concentrate that later can be

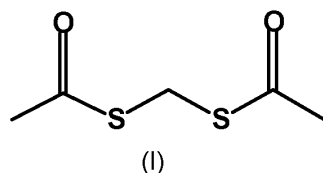
reformulated.

Although bis(acetylthio)methane could be considered structurally close to S,S- ethylidene dithioacetate that has been described as an active perfuming or flavoring ingredient in
5 US5871721, there was not any expectation of success that bis(acetylthio)methane could have perfuming properties since it is well known in the field of fragrances that it is very difficult to correlate olfactory properties with molecular structure because small structural differences can have a great and unpredictable impact in the activity of chemical compounds.

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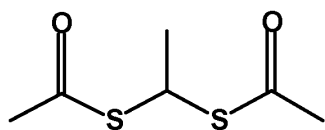
Furthermore, the olfactory properties of bis(acetylthio)methane (marijuana and green smell) are very different to the ones of S,S-ethylidene dithioacetate (tropical, sulfur odor, hints of garlic, onion, galbanum or bergamot notes, reminiscent of the bergamot leaf) and this difference in properties could not have been predicted by the structural difference of
15 the molecule. The fact that bis(acetylthio)methane has an unexpectedly high intensity odor, much higher than most of the known fragrance ingredients, is even less predictable, let alone, the impact of the sensory effect when applied to fragrances at very low dosages.

Thus, a first aspect of the present invention relates to the use of bis(acetylthio) methane
20 (BATM) as a fragrance ingredient, in particular, the fragrance ingredient has a marijuana smell and green smell. It has the following CAS registry number 1618-26-4 and the following formula (I):



25 As a fragrance ingredient, bis(acetylthio) methane may be used alone as olfactively active compound that exhibits such marijuana and green smell.

The inventors have also found that when S,S-ethylidene dithioacetate (SSED) of formula
(II) was added to the fragrance ingredient, a modulation in the smell was seen.
30 Minty/fresher notes appeared, and the "marijuana" character was described as more realistic.



(II)

Thus, the use of a combination of bis(acetylthio) methane and S,S-ethylidene
5 dithioacetate (SSED) of formula (II) as a fragrance ingredient is also part of the
invention. This use comprises either using a fragrance ingredient comprising both
components altogether, or using two separate fragrance ingredients for each single
component. The S,S-ethylidene dithioacetate acts modulating the smell of bis(acetylthio)
methane in the fragrance ingredient, providing to the fragrance a marijuana smell and
10 minty/fresher notes.

Another aspect of the present invention relates to a fragrance ingredient comprising
bis(acetylthio) methane and S,S-ethylidene dithioacetate. Both compounds act as
15 olfactively active compounds.

A further aspect of the present invention relates to a fragrance comprising at least two
fragrance ingredients, wherein one of the fragrance ingredients comprises bis(acetylthio)
methane, and optionally, other of the fragrance ingredients comprises S,S-ethylidene
dithioacetate. It also relates to a fragrance comprising at least two fragrance ingredients,
20 wherein one of the fragrance ingredients comprising bis(acetylthio) methane and S,S-
ethylidene dithioacetate altogether.

The fragrance ingredient according to the invention is suitable for perfumed products for
both fine perfumery and functional applications. Thus, a final aspect of the present
25 invention relates to a perfumed product comprising an effective perfuming amount of the
fragrance ingredient as defined above, more precisely, an effective perfuming amount a
fragrance ingredient which comprises bis(acetylthio) methane, optionally with an effective
perfuming amount of another fragrance ingredient which comprises S,S-ethylidene
dithioacetate, or alternatively, an effective perfuming amount of a fragrance ingredient
30 comprising bis(acetylthio) methane and S,S-ethylidene dithioacetate.

Brief Description of Drawings

FIG. 1 shows the curve dose-response of receptor TRPA1 and the mock. It represents
35 the variation of the fluorescence signal (activation of the receptor) when the concentration

of BATM increases in the media. For TRPA1 EC_{50} = 4.2 μ m and E_{max} from 11.7 μ m.

Detailed description of the invention

5 Definitions:

The term "olfactive active compound" as used herein is synonymous of "perfuming active compound" or "odor active compound" and refers to compounds that provide a desirable smell.

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The term "fragrance ingredient", which is also synonymous with the term "perfume ingredient" is understood as any individual material containing one or more olfactive active compounds to generate a desired pleasant effect. The fragrance ingredient may itself comprise many individual organic chemical compounds some of which may or may not be considered olfactive active compounds for the desired effect. For the purposes of the present invention, the fragrance ingredient comprises either bis(acetylthio)methane as the olfactively active compound, or bis(acetylthio)methane in combination with S,S-ethylidene dithioacetate as olfactively active compounds. These olfactive active compounds are the responsible of the desired pleasant odor of the fragrance according to the present

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invention.

The terms "fragrance" and "perfume" are used interchangeably herein, and they refer to a mixture of olfactively active compounds and, if desired, it may include auxiliary substances, such as additives or carriers. In the context of the present invention, the terms fragrance" and "perfume" refer to a mixture of the fragrance ingredients according to the present invention which may comprise other olfactively active compounds and also may include the auxiliary substances, such as additives or carriers.

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As used herein, "perfumed product" or "consumer product" means products intended to be used or consumed in the form as sold, and not for its subsequent modification of commercial manufacture or resale. The perfumed product according to the invention may be fine fragrances, air care products, cosmetic products, personal care products such as body sprays, detergents and laundry conditioners, carpet cleaners, air fresheners, textiles and soft furnishings, deodorizing or odor-removing products, odor control products, or scented items.

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The fragrance ingredient of the present invention is not intended for use in consumer products which are intended to be ingested such as foodstuffs or drinks, nor those which may be partially ingested as a result of the method of use such as in toothpaste or

mouthwashes, nor products which may be accidentally ingested such as chewing gum.

“An effective perfuming amount of a fragrance ingredient” as used herein refers to the amount of a fragrance ingredient that, when included in a consumer perfumed product provides the desired pleasant smell. The particular amount of the fragrance ingredient according to this invention will of course be determined by the particular consumer product in which it is to be included, being the fragrance ingredient, either an olfactively active compound alone or a combination of olfactively active compounds that provide the desired pleasant smell. In the context of the present invention the desired pleasant smell marijuana and green smell in the case that the fragrance ingredient comprises bis(acetylthio)methane alone or a marijuana smell and minty/fresher notes in the case that the fragrance ingredient further comprises S,S-ethylidene dithioacetate. Thus, in both cases, the fragrance ingredient of the present invention provides a characteristic marijuana smell.

The term “marijuana” as used herein refers to a variant of cannabis.

As mentioned above, the use of bis(acetylthio)methane as a fragrance ingredient forms part of the invention. As it is indicated in the examples the most repeated descriptors given by perfumers for this fragrance ingredient are marijuana, green, mocha, fresh, yeast/fermented, spicy, and leather. In a particular embodiment of the use, the fragrance ingredient exhibits marijuana and green smell. This aspect of the present invention may be formulated as a method for providing a marijuana and green smell to either a fragrance or to a perfumed product which comprises adding an olfactively effective amount of bis(acetylthio)methane as fragrance ingredient.

As illustrated in the examples, bis(acetylthio)methane (BATM) has the ability to activate trigeminal nerves. These nerves transmit somatosensory information from the face, including mouth and nasal cavities, to the brain. They are responsible for detecting sensations such as temperature, texture, or pain. These receptors can be activated by chemical compounds, this is known as chemesthesis or chemical touch which can significantly contribute to the overall smell experience. Specifically, the molecule has the ability to activate the trigeminal receptor TRPA1 (Transient Receptor Potential cation channel subfamily A, member 1), whose relationship with the generation of some somatosensory sensations in the nose and mouth, for instance tingling or pungency, has been described (see Nilius, Bernd; Flockerzi, Veit . (2014). [Handbook of Experimental Pharmacology] Mammalian Transient Receptor Potential (TRP) Cation Channels Volume 223 || TRPs in Taste and Chemesthesis (Chapter 5), 827–871). The compound can modulate the olfactory signal changing the smell experience. Besides, the compound has

high specificity and potency for TRPA1, with no off-target effects observed. This indicates that BATM can activate the trigeminal receptor TRPA1 related to tingly sensations in the nose (See Example 5).

- 5 Thus, in a particular embodiment of the use of bis(acetylthio) methane of formula (I) as a fragrance ingredient, in combination with any of the embodiments above or below, the bis(acetylthio) methane of formula (I) also acts activating the trigeminal receptor TRPA1 related to tingly sensations in the nose.
- 10 The compound also exerted an enhancement effect on freshness of different odorous materials, and also an enhancement effect on the olfactive intensity of different odorous materials, for instance, lemon oil, spearmint oil, clove oil, and basil oil. (see Examples 6 and 7).
- 15 Thus, in a particular embodiment of the use of bis(acetylthio) methane of formula (I) as a fragrance ingredient, the bis(acetylthio) methane of formula (I) produces an enhancing effect on freshness.

- 20 In another particular embodiment of the use of bis(acetylthio) methane of formula (I) as a fragrance ingredient, in combination with any of the embodiments above or below, the bis(acetylthio) methane of formula (I) produces an enhancing effect on the olfactive intensity of other odorous materials, or both. In a more particular embodiment, the odorous materials are selected from the group consisting of lemon oil, spearmint oil, clove oil, and basil oil.

- 25 The fragrance ingredient may further comprise S,S-ethylidene dithioacetate. Both this fragrance ingredient comprising bis(acetylthio)methane and S,S-ethylidene dithioacetate, as well as the use of a combination of bis(acetylthio)methane and S,S-ethylidene dithioacetate as fragrance ingredient, where the use comprises either using a fragrance
- 30 ingredient comprising both components altogether, or using two separate fragrance ingredients for each single component, are also part of the invention. This last aspect of the present invention may also be formulated as a method for providing a marijuana smell and minty/fresher notes to either a fragrance or to a perfumed product comprising adding an olfactively effective amount of bis(acetylthio)methane and of S-ethylidene dithioacetate
- 35 as a fragrance ingredient, wherein the method comprises using a fragrance ingredient comprising both components altogether or using two separate fragrance ingredients for each single component.

In a particular embodiment of the uses as defined above, the fragrance ingredients are encapsulated. Encapsulation can be used to protect ingredients from interactions with other ingredients in the product e.g., bleaches or to control the delivery of fragrances so that consumers have a better experience from using a product. Capsules containing the ingredient may be prepared by any of the commonly known techniques such as spray drying as described in WO2014118354, interfacial reaction such as amine aldehyde polycondensation reactions as described in US6261483, or free radical polymerization as described in EP2234712, or coacervation of oppositely charged polymers as described in US2800457.

Depending on the ratio of bis(acetylthio)methane and S,S-ethylidene dithioacetate, the fragrance ingredient has different notes, and while some of the ratios can be more appropriate for some perfumed products, other ratios can be more appropriate for other perfumed products. Therefore, this fragrance ingredient provides interesting olfactive notes, with the green/marijuana character being the main aspect, which can be further modulated with the ratio between both olfactively active compounds, as desired to generate other notes, like "spicy", "leather", "minty", "grapefruit" or "cassis".

In a particular embodiment, the fragrance ingredient comprising the combination according to the present invention is that wherein S,S-ethylidene dithioacetate is in a range from 5 to 95% of the total weight of the fragrance ingredient. In another particular embodiment, S,S-ethylidene dithioacetate is in a range from 5 to 17% of the total weight of the fragrance ingredient. In another particular embodiment, S,S-ethylidene dithioacetate is in a range from 10 to 12% of the total weight of the fragrance ingredient.

In a particular embodiment, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in weight ratio in the fragrance ingredient ranging from 19:1 to 1:19. In another particular embodiment, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in a weight ratio ranging from 7.5:1 to 1:7.5. In another particular embodiment, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in a weight ratio ranging from 7.5:1 to 1:6. In another particular embodiment, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in a weight ratio ranging from 7.5:1 to 1:1. In another particular embodiment of, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in weight ratio ranging from 6:1 to 1:1. In another particular embodiment, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in a weight ratio ranging from 7.5:1. In another particular embodiment, the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in a weight ratio 1:1.

The fragrance ingredient of the present invention comprising bis(acetylthio) methane

alone or further comprising S,S-ethylidene dithioacetate can be used for the creation of a very broad spectrum of fragrances by admixing it with other compounds with olfactory properties and, optionally, additives or carriers.

- 5 Either a fragrance comprising at least two fragrance ingredients, wherein one of the fragrance ingredients comprises bis(acetylthio) methane, and optionally, other of the fragrance ingredients comprises S,S-ethylidene dithioacetate, or alternatively, a fragrance comprising at least two fragrance ingredients, wherein one of the fragrance ingredients comprises bis(acetylthio) methane and S,S-ethylidene dithioacetate are part of the
10 invention.

In a particular embodiment, a fragrance according to the invention is that which comprises a fragrance ingredient comprising bis(acetylthio) methane as the sole olfactively active ingredient.

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In another particular embodiment, a fragrance according to the invention is that which comprises a fragrance ingredient comprising bis(acetylthio) methane as the sole olfactively active ingredient and another fragrance ingredient comprising S,S-ethylidene dithioacetate as the sole olfactively active ingredient.

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In another particular embodiment, a fragrance according to the invention is that which comprises a fragrance ingredient comprising bis(acetylthio) methane and S,S-ethylidene dithioacetate as the sole olfactively active ingredients.

- 25 In another particular embodiment, in combination with any of the embodiments indicated above the fragrance comprises appropriate additives or carriers.

The fragrances of the present invention may comprise further olfactively active compounds. A wide variety of olfactively active compounds are known for perfumery use,
30 including an extensive range of natural and synthetic products currently available such as alcohols, aldehydes, ketones, essential oils, ethers and acetals, esters, lactones, macrocycles, heterocycles, alkenes, ethers, nitriles, amines, oximes, ketals, thiols, thioketones, imines, etc. and mixtures thereof.

- 35 Without wishing to be limited, the chemical compounds comprising the ingredients of the perfume, generally have molecular weights of less than 325 atomic mass units, preferably less than 300 atomic mass units and more preferably less than 275 atomic mass units to ensure sufficient volatility to be noticeable. Furthermore, the compounds have molecular weights greater than 75 atomic mass units, preferably greater than 100 atomic mass units

as lower masses may be too volatile. It may further be preferred that each perfume ingredient has a boiling point in the range 80-400° C, such as in the range 100-350° C., when measured at 760 mm Hg. Ingredients of the fragrance do not contain strongly ionizing functional groups such as sulphonates, sulphates, or quaternary ammonium ions,
5 nor halogen atoms.

Fragrances of the present invention may optionally contain other natural extracts, such as essential oils. Natural extracts are produced by subjecting suitable natural materials such as plant components: leaves, flowers, seeds, roots or stems to an extraction process. The
10 extraction processes are well known to those skilled in the art. Essential oils can undergo additional processes to rectify and purify the oils for example by removing the terpene components via a "head cut" and/or removing the wax components via a "tail cut". Such natural extracts include but are not limited to those obtained from citrus species such as: lemons, oranges, mandarin, grapefruit, ugly fruit; from spices such as anise, cinnamon
15 clove, herbs such as basil, mint, lavender, lavandin, thyme, rosemary, or many varieties of plants such as geranium, various roses, citronella, cypress, eucalyptus, Peru balsam, camphor, sandalwood, ylang, cedarwood, and mixtures thereof.

Perfumes can be relatively simple in their composition with a minimum of two fragrance
20 ingredients, or they can comprise highly complex mixtures of natural and synthetic chemical compounds, chosen to provide any desired odor. For creativity it is preferred if the perfume composition contains more than 5 perfume ingredients, more preferable that perfume compositions contain more than 10 perfume ingredients. Perfume ingredients are well known in the art.

25 Without limitation examples of perfume ingredients include: hydrocarbons such as 3-carene; α -pinene; $\beta\beta$ -pinene; α -terpinene; γ -terpinene; p-cymol; bisabolene; camphene; caryophyllene; cedrene; farnesene; limonene; longifolene; myrcene; ocimene; valencene; or (E,Z)-1,3,5-undecatriene; aliphatic alcohols, such as hexanol; octanol; 3-octanol; 2,6-
30 dimethylheptanol; 2-methylheptanol, 2-methyloctanol; (E)-2-hexenol; (E)- and (Z)-3-hexenol; 1-octen-3-ol; mixture of 3,4,5,6,6-pentamethyl-3/4-hepten-2-ol and 3,5,6,6-tetramethyl-4-methyleneheptan-2-ol; (E,Z)-2,6-nonadienol; 3,7-dimethyl-7-methoxyoctan-2-ol; 9-decenol; 10-undecenol; 4-methyl-3-decen-5-ol; aliphatic aldehydes and acetals thereof such as hexanal; heptanal; octanal; nonanal; decanal; undecanal; dodecanal;
35 tridecanal; 2-methyloctanal; 2-methylnonanal; (E)-2-hexenal; (Z)-4-heptenal; 2,6-dimethyl-5-heptenal; 10-undecenal; (E)-4-decenal; 2-dodecenal; 2,6,10-trimethyl-5,9-undecadienal; heptanal diethyl acetal; 1,1-dimethoxy-2,2,5-trimethyl-4-hexene; citronellyloxyacetaldehyde; aliphatic ketones and oximes thereof such as 2-heptanone; 2-octanone; 3-octanone; 2-nonanone; 5-methyl-3-heptanone; 5-methyl-3-heptanonoxime;

- 2,4,4,7-tetramethyl-6-octen-3-one; aliphatic sulfur-containing compounds such as 3-methylthiohexanol; 3-methylthiohexyl acetate; 3-mercaptophexanol; 3-mercaptophexyl acetate; 3-mercaptophexyl butyrate; 3-acetylthiohexyl acetate; 1-menthene-8-thiol; aliphatic nitriles such as 2-nonenonitrile; 2-tridecenonitrile; 2,12-tri-decenonitrile; 3,7-dimethyl-2,6-
- 5 octadienonitrile; 3,7-dimethyl-6-octenenitrile; aliphatic carboxylic acids and esters thereof such as (E)- and (Z)-3-hexenyl formate; ethyl acetoacetate; isoamyl acetate; hexyl acetate; 3,5,5-trimethylhexyl acetate; 3-methyl-2-butenyl acetate; (E)-2-hexenyl acetate; (E)- and (Z)-3-hexenyl acetate; octyl acetate; 3-octyl acetate; 1-octen-3-yl acetate; ethyl butyrate; butyl butyrate; isoamyl butyrate; hexyl butyrate; (E)- and (Z)-3-hexenyl
- 10 isobutyrate; hexyl crotonate; ethyl isovalerate; ethyl-2-methyl pentanoate; ethyl hexanoate; allyl hexanoate; ethyl heptanoate; allyl heptanoate; ethyl octanoate; ethyl (E,Z)-2,4-decadienoate; methyl 2-octynoate; methyl 2-nonynoate; allyl 2-isoamyl oxyacetate; methyl 3,7-dimethyl-2,6-octadienoate; terpene alcohols such as citronellol; geraniol; nerol; linalool; lavadulol; nerolidol; farnesol; tetrahydrolinalool;
- 15 tetrahydrogeraniol; 2,6-dimethyl-7-octen-2-ol; 2,6-dimethyloctan-2-ol; 2-methyl-6-methylene-7-octen-2-ol; 2,6-dimethyl-5,7-octadien-2-ol; 2,6-dimethyl-3,5-octadien-2-ol; 3,7-dimethyl-4,6-octadien-3-ol; 3,7-dimethyl-1,5,7-octatrien-3-ol; 2,6-dimethyl-2,5,7-octatrien-1-ol; and formates, acetates, propionates, isobutyrate, butyrate, isovalerate, pentanoates, hexanoates, crotonates, tiglates, and 3-methyl-2-butenates thereof;
- 20 terpene aldehydes and ketones such as geranial; neral; citronellal; 7-hydroxy-3,7-dimethyloctanal; 7-methoxy-3,7-dimethyloctanal; 2,6,10-trimethyl-9-undecenal; geranyl acetone; and the dimethyl and diethyl acetals of geranial, neral, and 7-hydroxy-3,7-dimethyloctanal; cyclic terpene alcohols such as menthol; isopulegol; α -terpineol; terpinenol-4; menthan-8-ol; menthan-1-ol; menthan-7-ol; borneol; isoborneol; linalool
- 25 oxide; nopol; cedrol; ambrinol; vetiverol; guaial; and their formates, acetates, propionates, isobutyrate, butyrate, isovalerate, pentanoates, hexanoates, crotonates, tiglates, and 3-methyl-2-butenates; cyclic terpene aldehydes and ketones such as menthone; isomenthone; 8-mercaptopmenthan-3-one; carvone; camphor; fenchone; α -ionone; β -ionone; α -n-methylionone; β -ethylionone; α -isomethylionone; β -isomethylionone; α -irone;
- 30 α -damascone; β -damascone; β -damascenone; γ -damascone; δ -damascone; 1-(2,4,4-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; 1,3,4,6,7,8a-hexahydro-1,1,5,5-tetramethyl-2H-2,4a-methanonaphthalen-8(5H)-one; nootkatone; dihydronootkatone; α -sinensal; beta-sinensal; methyl cedryl ketone; cyclic alcohols such as 4-tert-butylcyclohexanol; 3,3,5-trimethylcyclohexanol; 3-isocamphylcyclohexanol; 2,6,9-trimethyl-(Z,Z,E)-
- 35 cyclododecatrien-1-ol; 2-isobutyl-4-methyltetrahydro-2H-pyran-4-ol; from the group of the cycloaliphatic alcohols for example α ,3,3-trimethyl-cyclohexyl methanol; 2-methyl-4-(2,2,3-trimethyl-3-cyclopent-1-yl)butanol; 2-methyl-4-(2,2,3-trimethyl-3-cyclopent-1-yl)-2-buten-1-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopent-1-yl)-2-buten-1-ol; 3-methyl-5-(2,2,3-trimethyl-3-cyclopent-1-yl)-pentan-2-ol; 3-methyl-5-(2,2,3-trimethyl-3-cyclopent-1-yl)-4-penten-2-ol;

- 3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopent-1-yl)-4-penten-2-ol; 1-(2,2,6-trimethylcyclohexyl)pentan-3-ol; 1-(2,2,6-trimethylcyclohexyl)hexan-3-ol; cyclic ethers such as cineol; cedryl methyl ether; cyclododecyl methyl ether; (ethoxymethoxy)cyclododecane; α -cedrene epoxide; 3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan; 3a-ethyl-6,6,9a-trimethyldodecahydronaphtho[2,1-b]furan; 1,5,9-trimethyl-13-oxabicyclo[10.1.0]trideca-4,8-diene; rose oxide; 2-(2,4-dimethyl-3-cyclohexen-1-yl)-5-methyl-5-(1-methylpropyl)-1,3-dioxane; cyclic ketones such as 4-tert-butylcyclohexanone; 2,2,5-trimethyl-5-pentylcyclopentanone; 2-heptylcyclopentanone; 2-pentylcyclopentanone; 2-hydroxy-3-methyl-2-cyclopenten-1-one; 3-methyl-cis-2-penten-1-yl-2-cyclopenten-1-one; 3-methyl-2-pentyl-2-cyclopenten-1-one; 3-methyl-4-cyclopentadecenone; 3-methyl-5-cyclopentadecenone; 3-methylcyclopentadecanone; 4-(1-ethoxyvinyl)-3,3,5,5-tetramethylcyclohexanone; 4-tert-pentylcyclohexanone; 5-cyclohexadecen-1-one; 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone; 9-cycloheptadecen-1-one; cyclopentadecanone; cyclohexadecanone; cycloaliphatic aldehydes such as 2,4-dimethyl-3-cyclohexenecarbaldehyde; 2-methyl-4-(2,2,6-trimethylcyclohexen-1-yl)-2-butenal; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarbaldehyde; 4-(4-methyl-3-penten-1-yl)-3-cyclohexenecarbaldehyde; cycloaliphatic ketones such as 1-(3,3-dimethylcyclohexyl)-4-penten-1-one; 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one; 2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl methyl ketone; methyl 2,6,10-trimethyl-2,5,9-cyclododecatrienyl ketone; tert-butyl 2,4-dimethyl-3-cyclohexen-1-yl ketone; esters of cyclic alcohols such as 2-tert-butylcyclohexyl acetate; 4-tert-butylcyclohexylacetate; 2-tert-pentylcyclohexyl acetate; 4-tert-pentylcyclohexyl acetate; decahydro-2-naphthylacetate; 3-pentyltetrahydro-2H-pyran-4-yl acetate; decahydro-2,5,5,8a-tetramethyl-2-naphthyl acetate; 4,7-methano-3a,4,5,6,7,7a-hexahydro-5- or -6-indenyl acetate; 4,7-methano-3a,4,5,6,7,7a-hexahydro-5- or -6-indenyl propionate; 4,7-methano-3a,4,5,6,7,7a-hexahydro-5- or -6-indenyl isobutyrate; 4,7-methanooctahydro-5- or -6-indenyl acetate; esters of cycloaliphatic carboxylic acids such as allyl 3-cyclohexyl propionate; allyl cyclohexyloxyacetate; methyl dihydrojasmonate; methyl jasmonate; methyl 2-hexyl-3-oxocyclopentanecarboxylate; ethyl 2-ethyl-6,6-dimethyl-2-cyclohexenecarboxylate; ethyl 2,3,6,6-tetramethyl-2-cyclohexenecarboxylate; ethyl 2-methyl-1,3-dioxolane-2-acetate; aromatic hydrocarbons such as styrene and diphenylmethane; araliphatic alcohols such as benzyl alcohol; 1-phenethyl alcohol; 2-phenethyl alcohol; 3-phenylpropanol; 2-phenylpropanol; 2-phenoxyethanol; 2,2-dimethyl-3-phenylpropanol; 2,2-dimethyl-3-(3-methylphenyl)propanol; 1,1-dimethyl-2-phenethyl alcohol; 1,1-dimethyl-3-phenylpropanol; 1-ethyl-1-methyl-3-phenylpropanol; 2-methyl-5-phenylpentanol; 3-methyl-5-phenylpentanol; 3-phenyl-2-propen-1-ol; 4-methoxybenzyl alcohol; 1-(4-isopropylphenyl)ethanol; esters of araliphatic alcohols and aliphatic carboxylic acids such as benzyl acetate; benzyl propionate; benzyl isobutyrate; benzyl isovalerate; 2-phenethyl

acetate; 2-phenethyl propionate; 2-phenethyl isobutyrate; 2-phenethyl isovalerate; 1-phenethyl acetate; α -trichloromethylbenzyl acetate; α , α -dimethylphenethyl acetate; α , α -dimethyl-phenethyl butyrate; cinnamyl acetate; 2-phenoxyethyl isobutyrate; 4-methoxybenzyl acetate; araliphatic ethers such as 2-phenethyl methyl ether; 2-phenethyl isoamyl ether; 2-phenethyl 1-ethoxyethyl ether; phenylacetaldehyde dimethyl acetal; 5 phenylacetaldehyde diethyl acetal; hydratropic aldehyde dimethyl acetal; phenylacetaldehyde glycerol acetal; 2,4,6-trimethyl-4-phenyl-1,3-dioxane; 4,4a,5,9b-tetrahyd roindeno[1,2-c1]-m-dioxin; 4,4a,5,9b-tetrahyd ro-2,4-dimethylindeno[1,2-d]-m-dioxin; aromatic and araliphatic aldehydes such as benzaldehyde; phenylacetaldehyde; 3-10 phenylpropanal; hydratropic aldehyde; 4-methylbenzaldehyde; 4-methylphenyl-acetaldehyde; 3-(4-ethylphenyl)-2,2-dimethylpropanal; 2-methyl-3-(4-isopropylphenyl)-propanal; 2-methyl-3-(4-tert-butylphenyl)propanal; 3-(4-tert-butylphenyl)propanal; cinnamaldehyde; α -butylcinnamaldehyde; α -amylcinnamaldehyde; α -hexylcinnamaldehyde; 3-methyl-5-phenylpentanal; 4-methoxybenzaldehyde; 4-hydroxy-3-15 methoxybenzaldehyde; 4-hydroxy-3-ethoxybenzaldehyde; 3,4-methylenedioxybenzaldehyde; 3,4-dimethoxybenzaldehyde; 2-methyl-3-(4-methoxyphenyl)propanal; 2-methyl-3-(4-methylenedioxyphenyl)propanal; aromatic and araliphatic ketones such as acetophenone; 4-methylacetophenone; 4-methoxyacetophenone; 4-tert-butyl-2,6-dimethylacetophenone; 4-phenyl-2-butanone; 4-20 (4-hydroxyphenyl)-2-butanone; 1-(2-naphthalenyl)ethanone; benzophenone; 1,1,2,3,3,6-hexamethyl-5-indanyl methyl ketone; 6-tert-butyl-1,1-dimethyl-4-indanyl methyl ketone; 142,3-dihydro-1,1,2,6-tetramethyl-3-(1-methylethyl)-1H-5-indenyllethanone; 5', 6', 7', 8'-tetrahydro-3', 5', 5', 6', 8', 8'-hexamethyl-2-acetonaphthone; aromatic and araliphatic carboxylic acids and esters thereof such as benzoic acid; phenylacetic acid; methyl 25 benzoate; ethyl benzoate; hexyl benzoate; benzyl benzoate; methylphenyl acetate; ethylphenyl acetate; geranyl phenyl acetate; phenethyl phenylacetate; methyl cinnamate; ethyl cinnamate; benzyl cinnamate; phenylethyl cinnamate; cinnamyl cinnamate; allyl phenoxyacetate; methyl salicylate; isoamyl salicylate; hexyl salicylate; cyclohexyl salicylate; cis-3-hexenyl salicylate; benzyl salicylate; phenylethyl salicylate; methyl 2,4-30 dihydroxy-3,6-dimethylbenzoate; ethyl 3-phenylglycidate; ethyl 3-methyl-3-phenylglycidate; nitrogen-containing aromatic compounds such as 2,4,6-trinitro-1,3-dimethyl-5-tert-butylbenzene; 3,5-dinitro-2,6-dimethyl-4-tert-butylacetophenone; cinnamonitrile; 5-phenyl-3-methyl-2-pentenitrile; 5-phenyl-3-methylpentanonitrile; methyl anthranilate; methyl N-methylantranilate; Schiff bases of methyl anthranilate with 35 7-hydroxy-3,7-dimethyloctanal, 2-methyl-3-(4-tert-butylphenyl)propanal or 2,4-dimethyl-3-cyclohexene-carbaldehyde; 6-isopropylquinoline; 6-isobutylquinoline; 6-sec-butylquinoline; indole; skatole; 2-methoxy-3-isopropylpyrazine; 2-isobutyl-3-methoxypyrazine; 4-(4,8-dimethyl-3,7-nonadienyl)pyridine; phenols, phenyl ethers and phenyl esters such as estragole; anethole; eugenol; eugenyl methyl ether; isoeugenol; isoeugenyl methyl ether;

thymol; carvacrol; diphenyl ether; β -naphthyl methyl ether; β -methyl ethyl ether; β -naphthyl isobutyl ether; 1,4-dimethoxybenzene; eugenyl acetate; 2-methoxy-4-methylphenol; 2-ethoxy-5-(1-propenyl)phenol; p-cresylphenyl acetate; from the group of the heterocyclic compounds, for example 2,5-dimethyl-4-hydroxy-2H-furan-3-one; 2-ethyl-4-hydroxy-5-methyl-2H-furan-3-one; 3-hydroxy-2-methyl-4H-pyran-4-one; 2-ethyl-3-hydroxy-4H-pyran-4-one; lactones such as 1,4-octanolide; 3-methyl-1,4-octanolide; 1,4-nonanolide; 1,4-decanolide; 8-decen-1,4-olide; 1,4-undecanolide; 1,4-dodecanolide; 1,5-decanolide; 1,5-dodecanolide; 1,15-pentadecanolide; cis- and trans-11-pentadecen-1,15-olide; cis- and trans-12-pentadecen-1,15-olide; 1,16-hexadecanolide; 9-hexadecen-1,16-olide; 10-oxa-1,16-hexadecanolide; 11-oxa-1,16-hexadecanolide; 12-oxa-1,16-hexadecanolide; ethylene-1,12-dodecandioate; ethylene-1,13-tridecandioate; coumarin; 2,3-dihydrocoumarin; or octahydrocoumarin.

In another particular embodiment, the fragrance further comprises appropriate carriers or additives. Appropriate carriers or additives refer to conventional additives or carriers used in fragrances. Examples of additives are surfactants, UV stabilizers, or antioxidants.

Examples of surfactants used to solubilize perfumes into some products include alcohol ethoxylates, sugar ethers and sugar esters, alkyl glycerides and amine oxides.

Examples of UV stabilisers include butyl methoxy dibenzoyl methane; bis ethyl-hexyloxyphenolmethoxyphenyl triazine; those sold under the Uvinol (registered trademark) trade name such as Uvinul D50 [bis(2,4-dihydroxyphenyl)-methanone], Uvinul MC80 (ethylhexyl methoxycinnamate) and Uvinul M40 (benzophenone-3); those sold under the Parsol (registered trademark) trade name, such as Parsol (registered trademark) MCX (same product as Uvinul MC80) and Parsol (registered trademark) 1789 (butyl methoxydibenzoylmethane); and those sold under the Tinogard (registered trademark) trade name, such as Tinogard (registered trademark) TT (pentaerythrityl tetra di-t-butyl hydroxyhydrocinnamate).

Examples of antioxidants include hindered phenols such as butylated hydroxy toluene, butylated hydroxyanisole, tocopherol and its derivatives such as α tocopheryl acetate (vitamin E) alkyl gallates such as propyl gallate, 3,5- ditertiary butyl-4-hydroxycinnamic esters.

Examples of appropriate carriers are solvents, for instance, alcohols such as ethanol, propanol, isopropanol, butanol, dipropylene glycol, diethyl phthalate, benzyl benzoate, isopropyl myristate, triacetin, and triethyl citrate (TEC). Other examples of suitable solvents include hydrocarbons such as those sold under the trade name Isopar

(registered trademark); ethers such as those sold under the Dowanol (registered trademark) trade name: benzyl benzoate; isopropyl myristate; dialkyl adipates; dialkyl succinates; dialkyl glutarates such as the dimethyl esters sold under the trade name Flexisolv (registered trademark); citrate esters, such as triethyl citrate and acetyl tributyl citrate; diethyl phthalate; diethylene glycol monoethyl ether; 3-methoxy-3-methyl-1-butanol; dipropylene glycol; and iso-propylidene glycerol sold under the Augeo (registered trademark) Clean Multi brand name.

These solvents may be used solely or in combination. Typically, the solvents have no or very low odor and make little contribution to the overall odor of the fragrance.

A perfumed product comprising an effective perfuming amount of the fragrance ingredient as defined above, more precisely, an effective perfuming amount a fragrance ingredient which comprises bis(acetylthio) methane, optionally with an effective perfuming amount of another fragrance ingredient which comprises S,S-ethylidene dithioacetate, or alternatively, an effective perfuming amount of a fragrance ingredient comprising bis(acetylthio) methane and S,S-ethylidene dithioacetate, is part of the invention.

The perfumed product can be selected from the group consisting of fine fragrances, air care products, cosmetic products, personal care products, detergents and laundry conditioners, household cleaners, carpet cleaners, air fresheners, textiles and soft furnishings, deodorizing or odor-removing products, odor control products, and scented items.

The amount of the fragrance ingredient according to the present invention (bis(acetylthio) methane alone or further comprising S,S-ethylidene dithioacetate) in the perfumed product may be selected based on the intended use of the perfumed product and the product's desired aroma. In a particular embodiment, the perfumed product according to the invention is that where fragrance ingredient according to the present invention is present in an amount equal to or lower than 10 ppm. In another particular embodiment, the perfumed product according to the invention is that where the fragrance ingredient is present in an amount equal to or lower than 5 ppm. In another particular embodiment, the perfumed product according to the invention is that where the fragrance ingredient is present in an amount equal to or lower than 1 ppm.

In another particular embodiment, the perfumed product according to the invention is that where the fragrance ingredient is present in an amount from 0.005 ppm to 10 ppm, particularly, 0.01-5 ppm. These amounts are effective amounts to provide the desired smell described for the fragrance ingredient of the present invention.

In a particular embodiment, the perfumed product according to the invention is that where the fragrance ingredient of the present invention is added in the form of a fragrance which comprises the fragrance ingredient together with further olfactively active compounds and, optionally, additives or carriers.

Such perfumed products include but are not limited to fine fragrances such as Eau De Parfum, colognes; household cleaning products; air care products; cosmetic products; personal care products; detergents and laundry conditioners; carpet cleaners; air fresheners such as plug-in air fresheners, aerosol products; textiles and soft furnishings; deodorizing or olfactively removing products; odor control products; and scented items.

A fine fragrance comprises fragrance ingredients in a solvent and is often applied to the skin by some form of spray applicator. More concentrated solutions of fine fragrance are termed Eau de Parfum which typically contains up to 20% of the fragrance composition. Eau de toilette typically contains up to 15% of the fragrance composition and body sprays typically contain up to 5%.

Specific examples of perfumed products are products for and/or methods relating to treating hair (human, dog, and/or cat), including, bleaching, coloring, dyeing, conditioning, shampooing, styling; products applied to skin including Eau de Parfum Eau de Toilette, colognes, body sprays, deodorants and antiperspirants; personal cleansing products such as bar soaps, liquid soap, shower gels, body washes and scrubs; leave on cosmetic products for skin care including application of creams, lotions, coloring cosmetics and other topically applied products; and shaving products.

Specific examples of personal care products are for instance shampoos, and hair conditioners, shower gels, body wash as exemplified), liquid soap, soap bars, deodorant spray, roll-on and stick deodorants as exemplified, moist wipes including baby wipes, flushable moist toilet tissues, skin cleansing or refreshing wipes. Formulations and ingredients of personal care products in which fragrances of the invention may be used are well known to those skilled in the art.

Fabric products include those for laundry detergency and garment care products such as powder, liquid and unit dose detergents, wash additives, fabric softeners, tumble drier sheets, ironing sprays and fabric fresheners; products for treating domestic soft furnishings such as carpet cleaners and malodor removers. Products for hard surfaces include manual and machine dishwashing products, hard surface cleaners for floors walls windows and mirrors and lavatory cleaners.

Specific examples of laundry detergents and conditioners include detergent powders, tablets, non-soap detergent bars and hard soap bars, concentrated detergent powders, liquid detergents, concentrated liquid detergents, non-aqueous liquid detergents and unit dosing liquid detergent sachets. Other post wash fabric treatments include tumble drier sheets or ironing waters. The formulation of laundry products is familiar to those skilled in the art.

Specific examples of household cleaners include liquid and spray hard surface cleaners which may be used directly on surfaces, liquids which can be diluted e.g., for floor cleaning or cleaning crockery and cooking utensils. Unit dosed solid or liquid sachet or tableted products such as for machine dishwashing and specialist cleaners for glass and mirrors. These products are available in a variety of product forms such as sprays, mousses, liquids, liquids containing suspended solids, impregnated wipes, sachets multicompartament sachets and unit dose devices. Bathroom sanitaryware cleaners include limescale cleaners, cistern blocks, rim blocks, liquid rim blocks and hybrid products.

Specific examples of air Care products to introduce fragrance to the ambient air in enclosed spaces such as rooms, vehicles, wardrobes, chests, drawers etc., may typically be in the form of sprays, candles, gels, membrane permeation devices, plug-in electrical devices, battery operated devices or liquid wick devices. Sprays may be aqueous or non-aqueous, pressurized with compressed gas or pump action. Candles and gels may be opaque, translucent or transparent and may be molded or packaged or contain additional ingredients to enhance their appearance. The plug-in and battery-operated devices may include devices that vaporize the fragrance by heat, evaporation, or nebulization.

Other products for freshening or fragrancng general ambient air countering malodours or repelling insects include devices which have no power source and work by diffusion e.g., through a polymeric membrane, or by electrical heating a wick in contact with a liquid reservoir so that the rate of fragrance can be controlled. Such devices can be electrically powered, so-called plug-in fresheners or battery powered so portable or for use in a motor vehicle.

Specific examples of carpet cleaners come in several forms: powders, liquids, foams and spray spot treatments. Many of these products have to be used in conjunction with a specific cleaning machine especially if large areas are to be treated. However, a desirable attribute of cleaning a carpet is to reduce malodors and leave a pleasant smell, such

products generally contain a fragrance. Malodor reducing fragrances of the present invention are both suitable and desirable for application in carpet cleaning products.

- 5 Bis(acetylthio) methane is a known compound that can be prepared for instance by reaction of diiodomethane with potassium thioacetate. An example for its preparation is disclosed in Example 1 of EP1090557.

- 10 S,S-ethylidene dithioacetate was originally found in blood oranges. The compound may be prepared by a condensation reaction between thioacetic acid and acetaldehyde. This synthesis is for instance described by L Sternson in "1,1-Bis(acylthio)alkanes Formed by Bae-Catalyzed Condensation of Thiol Acids", J. Org. Chem., 1978, vol. 43, No.23 where the condensation reaction between thioacetic acid and acetaldehyde is conducted in ether containing triethylamine or pyridine (see experimental section of the document).

- 15 The fragrance containing both bis(acetylthio) methane and S,S-ethylidene dithioacetate, as well as the perfumed product may be prepared by common techniques.

The fragrance comprising both olfactively active compounds can be prepared by admixing these compounds and, optionally, with other additives or carriers.

- 20 For the preparation of the perfumed product, bis(acetylthio) methane, can be incorporated in the perfumed product by admixing them with the rest of the components of the perfumed product.

- 25 When the perfumed product comprises both fragrances (bis(acetylthio) methane, and S,S-ethylidene dithioacetate), it can also be prepared by incorporating the fragrance ingredient comprising both bis(acetylthio) methane and S,S-ethylidene dithioacetate.

- 30 Throughout the description and claims the word "comprise" and variations of the word, are not intended to exclude other technical features, additives, components, or steps.

- Furthermore, the word "comprise" encompasses the case of "consisting of". Additional objects, advantages and features of the invention will become apparent to those skilled in the art upon examination of the description or may be learned by practice of the invention. The following examples are provided by way of illustration, and they are not intended to be limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein.
- 35

Examples

5 The percentages of the components in the fragrances may be determined by gas chromatography with FID detector.

ppm means part per million or mg/Kg.

Example 1: Odor thresholds

- 10 An indicator of the power of an odorant molecule is its odor threshold. The odor detection threshold is understood to be the lowest concentration of a certain odor compound that is perceivable by the human sense of smell.
- 15 The odor threshold value (OTV) of the molecule Bis(acetylthio)methane was calculated in the laboratory. Also, the odor threshold of ethylidene dithioacetate and other well-known perfumery molecules were assessed. The evaluation was done by following the European standard EN 13725:2003 guidelines and a GC-sniffing equipment. Each molecule was assessed at different concentration levels. The odor threshold value was the lowest
- 20 concentration detected by at least the 50% of panelists.

These were the calculated OTVs:

Molecule	Calculated OTV in air (µg / L)
Bis(acethylthio)methane	0.001
Ethylidene dithioacetate	0.01
Geraniol	2
Linalool	10
δ-Decalacone	0.09

- 25 The results indicated that BATM has a very low odor threshold, much lower than most common perfumery raw materials like linalool, geraniol or δ-decalactone. This means the smell of BATM is powerful enough to be detected at very low concentrations Ethylidene dithioacetate has a very low odor threshold too, despite it is ten times higher than the one of BATM.

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Example 2: Effect of bis(acetylthio)methane in fragrances at concentration below 1ppm

Bis(acetylthio)methane has a powerful smell so it can be used at much lower dosages compared to other raw materials and still have a sensory effect. A trial was designed to demonstrate that effect at a dosage below 1 part per million (mg/Kg). A triangular sensory test was carried out which results show that BATM has a significant influence in the perception of a fragrance smell when applied at 0.1 ppm.

Samples: Two fragrances with different olfactory profile were considered in this test:

- "Sidibou": Woody, sweet, oriental, profile (masculine)
- "Rouge Magic": Amber, rose, oakmoss profile (unisex)

Two versions of each fragrance were created:

- One with no further addition
- One containing 0.1 ppm (mg/kg) of >95% BATM

All these fragrances were applied in 96% ethanol at 20% giving a perfume application.

Triangular sensory test: The smell of each pair of versions (with and without BATM) was compared by means of a triangular test, a discrimination test to detect statistically significant sensory differences among samples. In this test, three coded (three-digit number) samples for each fragrance (Sidibou and Rouge Magic) were presented to each panelist. Two samples were the same and the other one was different. The panelists had to smell the samples by using a sniffing strip and mark the sample they perceive as different. Samples were presented in a random order to each panelist. 22 panelists did the evaluations.

Statistical data treatment: The number of right answers (the sample with a different composition were selected) was compared with tabulated values at 99% significance level. These tabulated values mark the minimum number of right answers to consider there were significant differences among samples at that significance level. Tabulated values are based in a χ^2 distribution which considers the expected number of right answers obtained by chance. These values are significance-level and number-of-panelist dependent.

Results: These are the number of right and wrong answers in the triangular test with the fragrance "Sidibou"

Right answers (The sample with a different composition is selected)	16
Wrong answers	6
Minimum number of right answers to demonstrate significant differences at 99%	14

Considering these results, significant differences (99% significance) were detected between the smell of the samples. Therefore, BATM at 0.1 ppm had a significant contribution to the smell of the "Sidibou" fragrance.

5

These are the number of right and wrong answers for the study with the fragrance "Rouge magic."

Right answers (The sample with a different composition is selected)	18
Wrong answers	4
Minimum number of right answers to demonstrate significant differences at 99%	14

- 10 Considering these results, significant differences (99% significance) were detected between the smell of the samples. Therefore, BATM at 0.1 ppm had a significant contribution to the smell of the "Rouge magic" fragrance.

- 15 Conclusion: This study shows that the molecule Bis(acetylthio)methane can exert a sensory effect when applied in a fragrance at 0.1ppm.

Example 3: Role of bis(acetylthio)methane in fragrances. An addition sensory test.

- 20 The objective of this study was to describe the role of Bis(acetylthio)methane when added to fragrances. For that, addition sensory tests were carried out.

Six very experienced evaluators (perfumers) were considered in this study. They had to describe the olfactive effect created with the addition of BATM. They smelt the same sample with and without 1ppm of BATM.

25

Then, they described the effect of the addition of BATM. Free use of any olfactive descriptor was allowed. These were the two sets of samples they had to compare:

- "Sidibou" fragrance vs Sidibou fragrance with 1ppm of BATM

- “Rouge Magic” fragrance vs Sidibou fragrance with 1ppm of BATM
The fragrances were applied in 96% ethanol at 20% giving a perfume application.
All samples were presented in the same dark, coded, 5ml containers to evaluators. They
wetted the tip of a sniffing strip in each sample and smelt them.

5

Results: These are summaries of the descriptors of the BATM role given by perfumers:

ADDITION	SENSORY EFFECT OF THE ADDITION
1 ppm BATM in Sidibou fragrance	Increase of the smell intensity (especially top notes). A more herbaceous, green, and fresh smell. Leather and marijuana notes are generated. On the other hand, sweet-balsamic notes are reduced
1 ppm BATM in Rouge Magic fragrance	Increase of the smell intensity (especially top notes). A fresh and herbal effect is generated. Woody note increased in quality and intensity. A more natural and complex smell is created

Conclusions: As can be seen the contribution of BATM in fragrances was described as
natural, fresh, herbal, marijuana, woody and leathery. Furthermore, a more intense smell,
especially for top notes, is noted when BATM is present.

Example 4: Improvement of the BATM perception when combined with ethylidene dithioacetate.

15

The benefits of the combination of BATM with ethylidene dithioacetate (ETA) were
explored. Different ratios were considered, from no presence of ethylidene dithioacetate to
an excess of it. A descriptive olfactive evaluation of each combination was carried out by
experienced perfumes.

20

Six very experienced evaluators (perfumers) participated in this study. They had to
describe the smell of 4 solutions of BATM combined with ethylidene dithioacetate (ETA) in
different ratios. Free use of any olfactive descriptor was allowed. The solutions were
prepared in triethyl citrate as a solvent. These were the samples they had to smell:

25

- BATM 10ppm (mg/kg) in TEC (ratio 1:0)
- BATM 10ppm + ETA 1.3ppm in TEC (ratio 7.5:1)
- BATM 10ppm + ETA 10ppm in TEC (ratio 1:1)
- BATM 10ppm + ETA 7.5ppm in TEC (ratio 1:7.5)

All samples were presented in the same dark, coded, 5ml containers to evaluators. They
wetted the tip of a sniffing strip in each sample and smelt them.

30

Results: This a compilation of the most repeated descriptors given by perfumers:

Ratio BATM:ETA	1:0	7.5:1	1:1	1:7.5
DESCRIPTORS	Marijuana	Marijuana (more realistic)	Marijuana (more realistic)	Marijuana
	Green	Green	Green (galbanum)	Less green (less natural)
	Mocha	Mocha	More intense mocha	More intense mocha
	Fresh	Fresher		
	Yeast / Fermented	Yeast / Fermented		
	Fermentation	Fermentation		
	Spicy (pepper, basil)	Spicy (pepper, basil)		
	Leather	Leather	Leather	
		Minty	Minty	Minty
			Sulphurous	Sulphurous
			Citrus	Citrus
			Tropical	Tropical
			Herbaceous	Herbaceous

- As can be seen, the molecule BATM alone presents descriptors like “marijuana”, “green”, “mocha”, “fresh”, “yeast / fermentation”, “spicy” and “leather”. When ethylidene dithioacetate was added in a low ratio, a modulation in the smell was seen. Minty/fresher notes appeared, and the “marijuana” character is described as more realistic. When the presence of ETA is increased to 1:1, the profile changes significantly. The smell, still perceived as “green” and “marijuana”, was considered less fresh. “Yeast /fermentation”, and “spicy” notes disappear. On the other hand, “sulphurous”, “citrus”, “tropical” and “herbaceous” were generated. The mocha note is empowered. When an excess of ETA is added, the smell was considered less green and less natural. The “marijuana” note was perceived as less realistic. The “leather” note was not perceived any more.
- Conclusions: This experiment demonstrated the combination of Bis(acetylthio)methane and Ethylidene dithioacetate gave several interesting olfactive notes which can be modulated with the combination ratio. Being the green/marijuana character the main aspect, other notes can be also generated, like “spicy”, “leather”, “minty”, “citrus” or “tropical”.

Example 5: Trigeminal nerves activation by bis(acetylthio)methane

Bis(acetylthio)methane (BATM) molecule was tested regarding its ability to activate trigeminal nerves. Specifically, the molecule was tested for its ability to activate the trigeminal receptor TRPA1 (Transient Receptor Potential cation channel subfamily A, member 1), whose relationship with the generation of some somatosensory sensations in the nose and mouth, for instance tingling or pungency, has been described.

This in-vitro assay was carried out by the laboratory Axxam (Milan, Italy). The measurement of receptor activation is based on imaging technique by using calcium-sensitive dyes and changes in fluorescence measurements.

HEK293 cells were transiently transfected with TRPA1 plasmid DNA or with a plasmid that didn't contain the sequence being tested. The last one, referred to as "mock" was a control to discard any effect of the substance in the experimental measurement different from the activation of the receptor. The transfection was done using Lipofectamine™ 2000 (Thermo Fisher Scientific) and then both groups of cells were seeded into 384-well plates. Cells were loaded with the calcium-sensitive dye Cal-520® AM (AAT Bioquest) and incubated at room temperature in the dark for 4 hours. Fluorescence responses were recorded using a FLIPR Penta plate reader following the injection of BATM. Data were analyzed by calculating the maximum and minimum fluorescence values, normalizing to baseline fluorescence ($\Delta F/F_0$), and generating dose-response (D/R) curves for the TRPA1 receptor and the mock or control.

Results: The curve dose-response of receptor TRPA1 and the mock are represented in FIG. 1. It represents the variation of the fluorescence signal (activation of the receptor) when the concentration of BATM increases in the media. The molecule BATM demonstrated strong, dose-dependent activation of TRPA1, with saturation observed between 3 mM and 10 μ M in the media, being the half maximal effective concentration (EC50) of 4.2 μ M. This value is close to the one generated by allyl isothiocyanate (4.2 μ M), a molecule known for generating a strong tingly sensation in the nose when smelt or tasted. Importantly, no unspecific activation was detected in mock-transfected cells, even at the highest concentrations. This indicates the compound's high specificity and potency for TRPA1, with no off-target effects observed. These results also indicate that BATM can activate the trigeminal receptor TRPA1 related to tingly sensations in the nose.

Example 6: Boosting effect of BATM on the perception of freshness of odorous materials

Sensory tests were carried out to confirm that the presence of BATM in an odorous mixture can boost the freshness sensation of the mixture.

5 Freshness is a very generic term in the field of perfumery. There have been studies addressing the definition of this descriptor (see M. Zarzo, “What is a Fresh Scent in Perfumery? Perceptual Freshness is Correlated with Substantivity” Sensors 2013, vol. 13, pp. 463-483). It is well known by perfumers that citrus and green notes are perceived as fresh. Also, some spicy notes can be considered fresh. Aquatic or aldehydic can also transmit a feeling of freshness. A special case is menthol (amongst others), with a smell
10 usually considered fresh, that can give a cooling effect through the activation of TRPM8 trigeminal receptors.

In this study, freshness was defined with the next concepts:

- a cooling / refreshing effect
- 15 - a fresh feeling derived from green / vegetal or citrus elements caused by the smell of the evaluated material

The study was done with two different sets: a composition of several fragrance materials and a single raw material, spearmint oil. The smell of both samples is considered as fresh
20 by perfumers. The amount of BATM added was low enough in order to maintain the main olfactive character of the original composition unchanged.

Samples:

- “Spice 1”: A spicy-smell composition.
- “Spice 2”: “Spice 1” (99.999%) + 0.001% of BATM
- 25 - “Spearmint 1”: Spearmint essential oil
- “Spearmint 2”: “Spearmint 1” (99.995%) + 0.005% of BATM

The composition of the samples was as follows (% w/w units):

Material	Spice 1	Spice 2	Spearmint 1	Spearmint 2
LEMON OIL	22.2	22.2	0	0
ORANGE OIL	7.8	7.8	0	0
CARDAMOM OIL	5.6	5.6	0	0
GINGER FRESH	7.8	7.8	0	0
CLOVE BUD OIL	4.4	4.4	0	0
LINALYL ACETATE	27.8	27.8	0	0
VETIVERYL ACETATE	13.3	13.3	0	0
AMBRETTOLIDE	11.1	11.2	0	0
SPEARMINT OIL	0	0	100.0	99.999
BATM	0	0.001	0	0.005

Each sample was diluted at 10% in ethanol 96% before the evaluation.

5 Evaluation method: Sniffing strips were wet in an ethanolic dilution of each sample and
panellist smelt them just after wetting. A group of non-experts evaluated the four samples
in two separate pairs. They smelt Spice 1 and Spice 2 compositions in one session and
Spear-mint 1 and Spear-mint 2 in another session. For each pair, they were asked to
answer this question: “What sample do you consider fresher?” (freshness defined in the
“Introduction” section). They had the possibility to select a third option: “no differences /
the same level of freshness”. A χ^2 test was applied to determine if a significant
10 enhancement was caused by the presence of BATM.

Results: The results for the “Spice” compositions were:

	Spice 1	Spice 2
Total number of panelists	14	
Number of panelists ranking the sample as more intense	2	10
Significance of the χ^2	0.979	

15 These results show that the addition of 0.001% (10ppm) of BATM to the composition
enhances the freshness feeling perceived by the panellists with a significance greater
than 95%.

The results for the “Spear-mint” compositions were:

20

	Spear-mint 1	Spear-mint 2
Total number of panelists	17	
Number of panelists ranking the sample as more intense	4	12
Significance of the χ^2	0.954	

These results show that the addition of 0.005% (50ppm) of BATM to the spear-mint oil
enhances the freshness feeling perceived by the panellists with a significance greater
than 95%

25

Conclusions: The study showed BATM can exert an enhancement of freshness given by the smell of some fragrance materials already considered fresh.

Example 7: Boosting effect of BATM on the olfactive intensity of odorous materials

5

Sensory tests were carried out to confirm that the presence of BATM can boost the intensity of the materials.

10 The study was done by combining BATM with four different fragrance materials: lemon oil, spearmint oil, clove oil and basil oil. The amount of BATM added was low enough to maintain the main olfactive character of the tested fragrance material unchanged.

Samples:

- Clove 1: 100% clove oil
- 15 - Clove 2: Clove 1 + 0.05% of BATM
- Spearmint 1: 100% Spearmint oil
- Spearmint 2: Spearmint 1 + 0.05% of BATM
- Lemon 1: 100% lemon oil
- Lemon 2: Lemon 2 + 0.05% BATM
- 20 - Basil 1: 100% basil oil
- Basil 2: Basil 1 + 0.05% BATM

Each sample was diluted at 10% in triethyl citrate before the evaluation.

25 Evaluation method: Sniffing strips were wet in the dilution of each sample and panelist smelt them just after wetting. A group of non-experts evaluated the samples in separated pairs, clove 1 and clove 2, spearmint 1 and spearmint 2, lemon 1 and lemon 2, basil 1 and basil 2. Each pair was smelt in a different session. For each pair, they were asked to answer this question: “What sample do you consider more intense?” They had the

30 possibility to select a third option: “the same level of intensity”. A χ^2 test was applied to determine if a significant intensity boost was caused by the presence of BATM.

Results: The results for the “clove” were:

	clove 1	clove 2
Total number of panelists	22	
Number of panelists ranking the sample as more intense	4	17

Significance of the χ^2	0.995
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*1 panelist didn't find different intensity between samples

- 5 These results show that the addition of 0.05% (500ppm) of BATM to the composition enhances the intensity of clove oil with a significance greater than 95%

The results for the "spearmint" were:

	spearmint 1	spearmint 2
Total number of panelists	22	
Number of panelists ranking the sample as more intense	3	15
Significance of the χ^2	0.995	

- 10 *4 panelists didn't find different intensity between samples

These results show that the addition of 0.05% (500ppm) of BATM to the composition enhances the intensity of spearmint oil with a significance greater than 95%

- 15 The results for the "lemon" were:

	lemon 1	lemon 2
Total number of panelists	23	
Number of panelists ranking the sample as more intense	6	15
Significance of the χ^2	0.950	

*2 panelists didn't find different intensity between samples

- 20 These results show that the addition of 0.05% (500ppm) of BATM to the composition enhances the intensity of lemon oil with a significance of 95%

The results for the "basil" were:

	basil 1	basil 2
Total number of panelists	22	

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Number of panelists ranking the sample as more intense	6	11
Significance of the χ^2	0.775	

*5 panelists didn't find different intensity between samples

These results show that the addition of 0.05% (500ppm) of BATM to the composition
5 doesn't enhance the intensity of basil oil with a significance greater than 95%

Conclusions: The study showed that BATM can exert a boost of the olfactive intensity of some fragrance raw materials. The extent of the effect may differ across a range of odour notes

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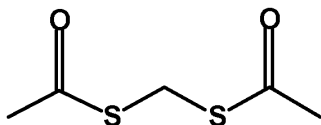
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Claims

1. Use of bis(acetylthio) methane of formula (I) as a fragrance ingredient.



5

(I).

2. Use according to claim 1, wherein bis(acetylthio) methane of formula (I) is used in combination with S,S-ethylidene dithioacetate as fragrance ingredient, wherein the use comprises either using a fragrance ingredient comprising both components altogether, or using two separate fragrance ingredients for each single component.

10

3. Use according to any of the claims 1-2, wherein the fragrance ingredients are encapsulated.

4. Use according to any of the claims 1-3, wherein the bis(acetylthio) methane of formula (I) activates the trigeminal receptor TRPA1 related to tingly sensations in the nose.

15

5. Use according to any of the claims 1-4, wherein the bis(acetylthio) methane of formula (I) produces an enhancing effect on freshness, on the olfactive intensity of other odorous materials, or both.

20

6. A fragrance ingredient comprising bis(acetylthio) methane and S,S-ethylidene dithioacetate.

7. The fragrance ingredient according to claim 6, wherein the bis(acetylthio) methane is in a range from 5 to 95% of the total weight of the fragrance ingredient.

25

8. The fragrance ingredient according to any of the claims 6-7, wherein S,S-ethylidene dithioacetate is in a range from 5 to 95% of the total weight of the fragrance ingredient.

9. The fragrance ingredient according to any of the claims 6-8, wherein the bis(acetylthio) methane and the S,S-ethylidene dithioacetate are in weight ratio ranging from 19:1 to 1:19.

30

10. A fragrance comprising at least two fragrance ingredients, wherein one of the fragrance ingredients comprises bis(acetylthio)methane, and optionally, other of the fragrance ingredients comprises S,S-ethylidene dithioacetate; or alternatively, one of the fragrance ingredients is as defined in any of the claims 6-9.

5

11. The fragrance according to claim 10, further comprising appropriate additives or carriers.

12. A perfumed consumer product comprising either an effective perfuming amount of a fragrance ingredient which comprises bis(acetylthio) methane, optionally with an effective perfuming amount of another fragrance ingredient which comprises S,S-ethylidene dithioacetate, or alternatively, an effective perfuming amount of a fragrance ingredient as defined in any of the claim 4-7.

13. The perfumed consumer product according to claim 12, wherein the fragrance ingredient is present in an amount equal to or lower than 10 ppm with respect to the total weight of the perfumed product.

14. The perfumed consumer product according to claim 13, wherein the fragrance ingredient is present in an amount equal to or lower than 1 ppm with respect to the total weight of the perfumed product.

15. The perfumed consumer product according to claim 12, wherein the fragrance ingredient is added in the form of a fragrance as defined in any of the claim 10-11.

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