

Description

Usnic acid, a natural well-known antimicrobial agent, has been demonstrated to be extremely effective against Gram-positive bacteria, fungi, and yeast with Minimum Inhibitory Concentrations as low as 10 ppm for certain species [M. Fontana, G. Proserpio, Riv. Ital. Essenze, Profumi, Piante Off., Aromi, Saponi, Cosmetici, Aerosol (RIPOAM), 1974, 56, 315-336]. The use of free usnic acid in cosmetic formulations is complicated due to its insolubility in all commonly used solvent systems [H. Bergerhausen, Cosmetics and Toiletries 1976, 91, 25-26; Manufacturing Chemist 1989, 22-27]. Soluble derivatives of usnic add, such as its alkali and ammonium salts, as well as certain esters, have been reported [Handelsgesellschaft Schlosser GmbH, 1975, Ger. Offen. 2354517. Orissa Drebing GmbH, 1975, Ger. Offen. 2351927. Orissa Drebing GmbH, 1975, Ger. Offen. 2351864. Orissa Drebing GmbH, 1976, Ger. Offen. 2432484.]. The major drawbacks of these derivatives are their insufficient stability properties, such as decolorization, pH-sensitivity, and reduction of antimicrobial activity.

Usnic add [C₁₈H₁₆O₇, 2,6-Diacetyl-7,9-dihydroxy-8,9b-dimethyl-1,3(2H,9bH)-dibenzofurandione] exhibits the following characteristics:

MW 344.32; mp 201-203 °C, [α]_D +488° (c 0.4, CHCl₃); mp 204 °C, [α]_D +509.4° (c 0.697, CHCl₃);

Solubility at 25 °C (g/100 ml): water <0.01, acetone 0.77, ethyl acetate 0.88, ethanol 0.02, chloroform 4.6, pyridine 2.12, benzene 0.94, dioxane 0.99, isopropyl alcohol 0.28, propylene glycol <0.01, dipropylene glycol 0.01, diethyl phthalate 0.45.

Certain perfumery raw materials now have been found to solubilize usnic add - and leading to stable solutions. This finding allows the direct use of usnic add, this natural antimicrobial agent isolated from alpine lichen, in numerous types of perfumes, cosmetic and toiletry formulations, without the usually required derivatization to improve its solubility.

The natural and synthetic perfumery raw materials are all characterized by exhibiting an aromatic ring. In the foreground of the interest are such standard perfumery materials as:

benzyl salicylate (1), benzyl benzoate (2), anisic aldehyde (3), isoeugenol methylether (4), cinnamyl acetate (5), and eugenol (6).

These perfumery raw materials exhibiting the desired solubilizing property are thus not only odorants, but also fixatives, blenders and modifiers.

The amount of any of (1) to (6) in the perfume bases is not too critical. Convenient amounts are:

20 to 90% of any of (1) to (6). Mixtures of any one of (1) to (6) are also possible.

The maximum solubility (g/100 ml) of pure usnic add in the above pure compounds (1) to (6) at 25 °C is:

benzyl salicylate 3.01, benzyl benzoate 1.93, anisic aldehyde 4.06, isoeugenol methylether 2.69, cinnamyl acetate 1.60, eugenol 2.18, anethol 4.30.

Examples

Three formulae of perfume compositions containing different concentrations of free usnic add are listed below:

Formula 1.	
Compound	wt. %
Usnic Acid	0.5
1	20.0
2	18.0
6	2.0
Linalool	8.0
Benzyl Acetate	8.0
Hexyl Cinnamic Aldehyde	13.5
Phenyl Ethyl Alcohol	2.0
Hydroxycitronellal	4.0
Ylang Ylang Oil	2.0
Aldehyde C-14	6.0
Aldehyde C-18	6.0
Methyl Anthranilate	4.0
Indolene-50 [8,8-bis-(3H-indol-3-yl)-2,6-dimethyl-2-octanal 50% in castor oil]	2.0
Methyl Salicylate	4.0
	100.00

Formula 2.	
Compound	wt. %
Usnic Acid	1.50
1	70.0
2	7.0
4	0.30
Linalool	1.00
Benzyl Acetate	7.00
Linalyl Acetate	0.70
Hexyl Cinnamic Aldehyde	2.30
Phenyl Ethyl Alcohol	3.00
Hydroxycitronellal	5.70
Geraniol Extra	0.30
Cinnamic Alcohol	0.15
Aldehyde C-14 (10% in DEP)	0.15
Aldehyde C-16 (10% in DEP)	0.15
Aldehyde C-18 (10% in DEP)	0.30
Argeol [hydroxycitronellal-methyl anthranilate Schiff base]	0.15
α -Ionone	0.30
	100.00

Formula 3.	
Compound	wt. %
Usnic Acid	2.00
1	85.0
2	0.80
6	0.20
Linalool	0.80
Phenyl Ethyl Alcohol	6.70
Geraniol Extra	0.90
Citronellol Extra	0.90
Geranyl Acetate	0.90
Phenyl Aethyl Acetate	0.80
Diphenyl Oxide (10% in DEP)	0.01
Aldehyde C-9 (10% in DEP)	0.02
Aldehyde C-18 (10% in DEP)	0.02
Methyl Ionantheme-100 [α -methyl ionone] (10% in DEP)	0.02
Iso Menthone (10% in DEP)	0.08
Rose Oxide (10% in DEP)	0.04
Methyl Octine Carbonate (10% in DEP)	0.01
Phenyl Aethyl Phenyl Acetate	0.80
	100.00

Perfume compositions containing free usnic acid can thus be readily incorporated in the usual manner and using the well-known techniques into perfumed consumer products, e.g. into a wide variety of cosmetic and toiletry formulations, such as deodorants, antiperspirants, shower gels, soaps, sanitary pads, skin creams, lotions, tooth paste, mouth wash, etc. Such tooth paste may contain the usual ingredients such as abrasives, surfactants, humectants, binders, therapeutic ingredient(s), if necessary, anti tartar ingredients, preservatives, whiteners, etc.

Two example formulations of applications in a deodorant stick and a deodorant non-aerosol spray are given below.

Deodorant Stick:

Propylene glycol	63.00%
Sodium stearate	5.00%
Deionized water	25.00%
Hydroxyethylcellulose (Natrosol 250)	0.20%
Isostearamidopropyl PG diethyl ammonium chloride (Lexquat AMG-IS)	2.00%
Lauramide DEA (Standamid LD>)	4.00%
Formula 1 (or 2, or 3)	0.80%
	100.00%

Non-Aerosol Deodorant Spray:

Propylene glycol	3.00%
Water	20.50%
Ethanol	75.00%
Formula 1 (or 2, or 3)	1.50%
	100.00%

Shower gel:

Conventional shower gels, such as described in

Cosmetic & Toiletries 104 (1989), 84 seq., in particular 86, or in

Cosmetic & Toiletries 99 (1984) 96

may contain for example 0,80 parts and 3,00 parts per weight, respectively, of Fragrance Formula 1 (or 2, or 3)

Tooth paste:

Calcium carbonate	50.00%
Sodium lauryl sulphate	1.50%
Glycerol	10.00%
Sorbitol	15.00%
Gum tragacanth	1.50%
Sodium monofluorophosphate	0.90%
Tetrasodium pyrophosphate	0.25%
Zinc citrate trihydrate	0.50%
Saccharin	0.10%
Formaldehyde (40%)	0.06%
anethol based perfume or flavour	1.00%
Water to	100.00%

The usnic add in anethol is conveniently ca. 1.5 to 2.5% per weight.

Claims

1. Perfume base, containing usnic acid and a perfumery raw material exhibiting an aromatic ring.
2. Perfume base according to claim 1, wherein the perfumery raw material is selected from the group consisting of benzyl salicylate, benzyl benzoate, anisic aldehyde, isoeugenol methylether, cinnamyl acetate, eugenol and anethol.
3. Perfume base according to claim 1, wherein the perfumery raw material is selected from the group consisting of benzyl salicylate, benzyl benzoate, anisic aldehyde, isoeugenol methylether, cinnamyl acetate and eugenol.
4. Perfume base according to claim 1, 2 or 3, wherein the concentration of usnic add is 0.3% w/w to 3% w/w, preferably 0.5% w/w to 2% w/w.
5. The use of a perfumery raw material exhibiting an aromatic ring, as a solubilizing agent for usnic add.
6. The use of benzyl salicylate, benzyl benzoate, anisic aldehyde, isoeugenol methylether, cinnamyl acetate, eugenol and anethol according to claim 5.
7. The use of benzyl salicylate, benzyl benzoate, anisic aldehyde, isoeugenol methylether, cinnamyl acetate and eugenol according to claim 5.

Patentansprüche

1. Parfümbase, enthaltend Usninsäure und ein Rohmaterial für parfümistische Zwecke, das einen aromatischen Ring aufweist.
2. Parfümbase gemäss Anspruch 1, dadurch gekennzeichnet, dass das Parfümrohmaterial aus der Gruppe Benzylsalicylat, Benzylbenzoat, Anisaldehyd, Isoeugenolmethylether, Zimtsäureacetat, Eugenol und Anethol ausgewählt ist.



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5. The use of a perfumery raw material exhibiting an aromatic ring, as a solubilizing agent for usnic add.
6. The use of benzyl salicylate, benzyl benzoate, anisic aldehyde, isoeugenol methylether, cinnamyl acetate, eugenol and anethol according to claim 5.
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3. Parfümbase gemäss Anspruch 1, dadurch gekennzeichnet, dass das Rohmaterial aus der Gruppe Benzylsalicylat, Benzylbenzoat, Anisaldehyd, Isoeugenolmethylether, Zimtsäureacetat und Eugenol ausgewählt ist.
- 5 4. Parfümbase gemäss Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass die Konzentration an Usninsäure zwischen 0.3% (G/G) und 3% (G/G), Vorzugsweise zwischen 0.5% (G/G) und zwischen 2% (G/G) liegt.
- 10 5. Verwendung eines Rohmaterials für parfümistische Zwecke mit aromatischem Ring, als Solubilisierungsmittel für Usninsäure.
6. Verwendung von Benzylsalicylat, Benzylbenzoat, Anisaldehyd, Isoeugenolmethylether, Zimtsäureacetat, Eugenol oder Anethol gemäss Anspruch 5.
- 15 7. Verwendung von Benzylsalicylat, Benzylbenzoat, Anisaldehyd, Isoeugenolmethylether, Zimtsäureacetat oder Eugenol gemäss Anspruch 5.

Revendications

- 20 1. Base parfumée contenant de l'acide usnique et une matière première de parfumerie présentant un anneau aromatique.
2. Base parfumée selon la Revendication 1, dans laquelle la matière première de parfumerie est sélectionnée parmi le groupe composé de salicylate de benzyle, de benzoate de benzyle, d'aldéhyde anisique, de méthyléther d'isoeugénol, d'acétate de cinnamyle, d'eugénol et d'anéthol.
- 25 3. Base parfumée selon la Revendication 1, dans laquelle la matière première de parfumerie est sélectionnée parmi le groupe composé de salicylate de benzyle, de benzoate de benzyle, d'aldéhyde anisique, de méthyléther d'isoeugénol, d'acétate de cinnamyle et d'eugénol.
- 30 4. Base parfumée selon la Revendication 1, 2 ou 3, dans laquelle la concentration en acide usnique est comprise entre 0,3 % en masse et 3 % en masse, de préférence entre 0,5 % en masse et 2 % en masse.
- 35 5. L'utilisation d'une matière première de parfumerie présentant un anneau aromatique en tant qu'agent de solubilisation de l'acide usnique.
6. L'utilisation de salicylate de benzyle, de benzoate de benzyle, d'aldéhyde anisique, de méthyléther d'isoeugénol, d'acétate de cinnamyle, d'eugénol et d'anéthol selon la Revendication 5.
- 40 7. L'utilisation de salicylate de benzyle, de benzoate de benzyle, d'aldéhyde anisique, de méthyléther d'isoeugénol, d'acétate de cinnamyle et d'eugénol selon la Revendication 5.
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