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(71) Applicant (for all designated States except US): **GIVAUDAN SA** [CH/CH]; Chemin de la Parfumerie 5, CH-1214 Vernier (CH).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **DANIHER, Andrew** [US/US]; 3406 Walworth Avenue, Cincinnati, OH 45226 (US).

(74) Agent: **McSTEa, John, Anthony**; Givaudan Schweiz AG, Global Patents, Überlandstrasse 138, CH-8600 Dübendorf (CH).

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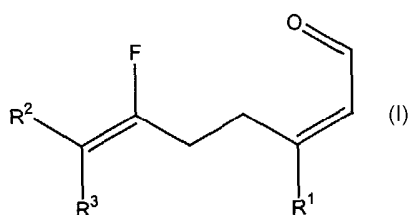
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(54) Title: IMPROVEMENTS IN OR RELATED TO ORGANIC COMPOUNDS



(57) Abstract: A flavour or fragrance composition comprising a compound of formula (I) and method of flavouring or of adding fragrance to a food, beverage or consumer product or household product using these compounds R¹, R² and R³ are independently hydrogen, methyl or ethyl.

Improvements in or related to organic compounds

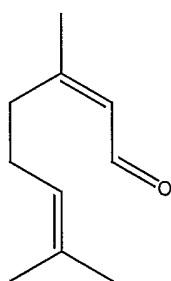
The invention relates to flavour or fragrance compositions containing 6-fluoro-alkenes, in particular substituted 6-fluoro-2,6-heptadienals and to methods of flavouring or of adding fragrance to a food, beverage or a consumer product or household product using these compounds.

The flavour and fragrance industry is continuously interested in new ingredients that may impart to a product a green, lemony and citral-like character.

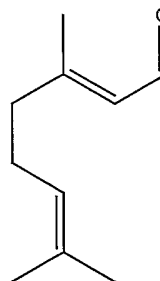
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3,7-dimethyl-2,6-octadienal, well known as citral, a mixture of neral and geranial, is an important ingredient in the flavour industry and has found use in flavour compositions to impart citrus notes. However, the use of citral in the flavour industry is limited to products that do not have a low pH value, because of its instability under such conditions whereupon it degrades into aromatic ring systems, e.g. p-cresol, p-cymene and p-methylaceto-phenone, described for example by Schieberle et al. (Lebensm.-Wiss. u- Technol., 21, 158-162, 1988). These degradation products are responsible for undesirable off-notes in food products that lead to the reduction of the flavour quality.

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neral



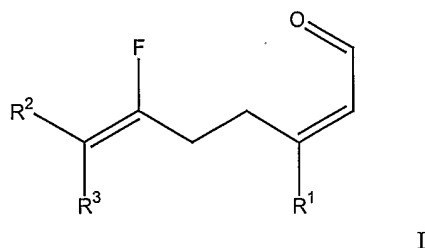
geranial

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Surprisingly, we have now found that substituted 6-fluoro-2,6-heptadienals are very stable under acidic conditions, e.g. under conditions wherein the pH value is below 7, in particular below 4, particularly below 3. In addition these compounds show similar organoleptic properties as citral.

25

Accordingly, the invention provides in one of its aspects a flavour or fragrance composition comprising a compound of formula I



wherein R^1 , R^2 and R^3 are independently hydrogen, methyl, or ethyl.

Particularly preferred are compositions according to the invention comprise 6-fluoro-3,7, dimethyl-2,6-octadienal (i.e. R^1 , R^2 and R^3 = methyl).

Accordingly, compounds of formula I may find use in particular in acidic flavour and fragrance applications to achieve a constant flavour quality over a long period of time, e.g. up to 10 days, more preferably up to 100 days, without degrading into undesirable off-notes.

The compounds of formula I may contain one or more prochiral centres and as such may exist as a mixture of cis-trans-isomers, or they may be resolved as isomerically pure forms. Resolving stereoisomers adds to the complexity of manufacture and purification of these compounds and so it is preferred to use the compounds as mixtures of their stereoisomers simply for economic reasons. However, if desired to prepare individual stereoisomers, this may be achieved according to methodology known in the art, e.g. column chromatography.

In a further aspect the present invention refers to food products comprising a compound of formula I. Particular preferred are acidic food products such as beverages, e.g. carbonated soft drinks and juice drinks, such as lemon juice, orange juice or lime juice.

In a food product, a compound of formula I may be present in amounts ranging from 0.001 to 100 ppm, more preferably from 0.01 to 10 ppm, most preferred 0.1 to 7 ppm. A compound of formula I or a mixture thereof may be added to a food product alone or by adding a flavour or fragrance composition comprising a compound of formula I to a food product. The compounds of formula I are particularly well suited in flavour or fragrance

compositions where enhancement of citrus notes are required, such as lemon, orange and lime compositions.

In a further aspect the present invention refers to fragrance applications, e.g. any field
5 of fine and functional perfumery, such as perfumes, household products, laundry products, body care products and cosmetics, comprising a compound of formula I or in combination with other known odourant molecules selected from the extensive range of natural and synthetic molecules currently available, such as essential oil, alcohols, aldehydes and ketones, ether and acetals, ester and lactones, macrocycles and
10 heterocycles, and/or admixtures with one or more ingredients or excipients conventionally used in conjunction with odourants in fragrance compositions, for example carrier materials, and other auxiliary agents commonly used in the art.

In fragrance applications compounds of the present invention may be present in
15 amounts ranging from 0.001 to 20 weight percent depending upon the specific application and on the nature and quantity of other odourant ingredients.

6-fluoro-2,6-heptadienals may be synthesised starting from an appropriate fluorinated ester by Claisen rearrangement followed by Cope rearrangement, as described for
20 example by F. Camps et al., Tetrahedron Vol. 44, No. 16, pp. 5161 – 5167, 1988. The resulting fluorinated acid may then be reduced to the corresponding fluorinated alcohol in the presence of LiAlH_4 , which may further converted to the corresponding fluorinated aldehyde in the presence of MnO_2 , as described for example by C. Arbonés et al., Heterocycles, Vol. 31, No. 1, pp 67 – 78, 1990.

25 The following example is set forth to illustrate the invention. This example is illustrative only and is not intended to limit the scope of the invention in any way.

Example 1:

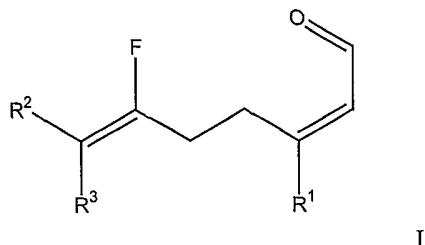
30 The acid stability of 6-fluoro-3,7-dimethyl-2,6-octadienal (6-F-citral) is tested in direct comparison to citral. 200 ppm solutions of 6-F-citral and citral in an acid (pH 2.8) beverage base is made. The solutions is stored at room temperature in the dark for 111 days. Time points are analyzed by Fast-GC using an internal standard to quantify
35 the amounts of each compound. Within 20 days, all of the citral is degraded. In

contrast, no degradation of 6-F-citral is detected. Even after 111 days, 6-F-citral is just about 100 % intact, accordingly no degradation of 6-F-citral occurs.

5 It should be understood that the embodiments of the present invention shown and described in the specification are only preferred embodiments of the inventors who are skilled in the art and are not limiting in any way. Therefore, various changes, modifications or alterations to these embodiments may be made or resorted to without departing from the spirit of the invention and the scope of the following claims.

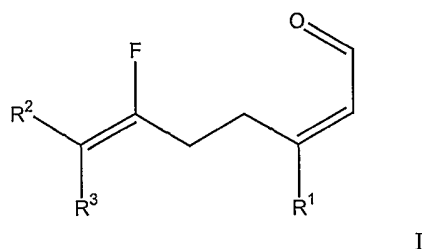
What is claimed:

1. A flavour or fragrance composition comprising a compound of formula I



wherein R^1 , R^2 and R^3 are independently hydrogen, methyl, or ethyl.

2. A composition according to claim 1 wherein R^1 , R^2 and R^3 is methyl.
3. A food product comprising a compound of formula I as defined in claim 1 from about 0.001 to 100 ppm.
4. A food product according to claim 3 characterised in that the food product has a pH value below 7.
5. A food product according to claim 3 characterised in that the food product is a beverage.
6. The use of a compound of formula I as defined in claim 1 in beverages.
7. A method of manufacturing a food product, comprising the incorporation of a compound of formula I



wherein R^1 , R^2 and R^3 are independently hydrogen, methyl, or ethyl.

8. A method of imparting or enhancing a citrus note to a food product by adding a compound of formula I thereto.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CH 03/00554

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A23L1/226 A23L1/235 C07C45/00 A61K7/46

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)

IPC 7 A23L C07C A61K

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 3 654 309 A (THOMAS ALAN FRANCIS) 4 April 1972 (1972-04-04) column 3, line 55 -column 4, line 49 --- -/--	1-8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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