

FLAVOUR INGREDIENTS COMPRISING ETHYL-4.8-DECADIENOATE

5 TECHNICAL FIELD

[0001] The present disclosure relates to flavour ingredients and methods of making. More particularly, the present disclosure relates to flavour compositions and beer-type beverages comprising the flavour ingredients. Even more particularly, the present disclosure relates to the use of flavour ingredients for imparting natural, fruity, pear-like character of hops to a beer-type
10 beverage.

BACKGROUND

[0002] Hops are critical components in beer flavour. A traditional method for producing beer is to obtain a wort by mixing malt and water (if necessary, secondary raw materials such as starchy grains), decomposing the malt starch into sugars while allowing enzymes present in the
15 malt (mainly amylase and protease) to act thereon at about 40°C to 75°C, and filtering. Hops are added thereto to impart a characteristic aroma and bitter taste to beer, the malting enzyme is stopped by boiling, filtered, further cooled, yeast is added, yeast fermentation is performed at a low temperature producing alcohol and modifying the flavour, yeast is removed by filtration, and then the mixture is aged at a low temperature.

20 [0003] Diversification of consumer preferences in recent years has created a desire for the development of low or non-alcoholic beer-type beverages having various aromas and taste characteristics. Non-alcoholic beer flavored beverages have long been produced by a dealcoholization method such as vacuum distillation, but recently developed products have become predominant in which bitter materials, body materials, sugar materials, sour materials,
25 hop extracts, hops flavours, carbonic acids, and the like are formulated. However, because the extract component of hops is not aged for a long period of time by this formulation, the flavour of beer is still insufficient compared to natural hops contained in beer.

[0004] Accordingly, there remains a need to provide flavour ingredients which are natural, mild, strong, and capable of imparting a hop-flavour by adding the flavour ingredient to a
30 step of blending a beer-type beverage, particularly a non-alcoholic beer-type beverage, or a step after fermentation or aging of a beer-type alcohol beverage.

SUMMARY OF ILLUSTRATIVE EMBODIMENTS

- [0005] In one illustrative embodiment, a flavour composition comprises one or more decadienoate ester compounds selected from the group consisting of ethyl (4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z) decadienoate and combinations thereof; and one or more further flavour ingredients.
- [0006] In another illustrative embodiment, a beer-type beverage comprises one or more decadienoate ester compounds selected from the group consisting of ethyl (4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z) decadienoate and combinations thereof; and a product base.
- [0007] In yet another illustrative embodiment there is provided a use of one or more decadienoate ester compounds selected from the group consisting of ethyl (4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z) decadienoate and combinations thereof, as an ingredient to confer, enhance, improve or modify the hops taste of a beer-type beverage.
- [0008] These and other features, aspects and advantages of specific embodiments will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

- [0009] The following text sets forth a broad description of numerous different embodiments of the present disclosure. The description is to be construed as exemplary only and does not describe every possible embodiment since describing every possible embodiment would be impractical, if not impossible. It will be understood that any feature, characteristic, component, composition, ingredient, product, step or methodology described herein can be deleted, combined with or substituted for, in whole or part, any other feature, characteristic, component, composition, ingredient, product, step or methodology described herein. Numerous alternative embodiments could be implemented, using either current technology or technology developed after the filing date of this patent, which would still fall within the scope of the claims. All publications and patents cited herein are incorporated herein by reference.
- [0010] The present disclosure relates to the surprising finding that certain specific isomers of decadienoate esters exhibit a more powerful “fruity-pear” character enabling the creation of more authentic hop flavours by the use of these specific isomers as flavour ingredients. In particular, the present disclosure relates to the surprising finding that the flavour ingredients

described herein can be used to provide a beer-type beverage with an improved hop flavour and taste profile typically associated with regular beer.

[0011] In one embodiment, the flavour ingredients according to the present disclosure may be added to a flavour composition for use in a consumable. Broadly, consumables include, but are not limited to, comestibles of all kinds, confectionery products, baked products, sweet products, savoury products, fermented products, dairy products, non-dairy products, beverages, nutraceuticals, and pharmaceuticals.

[0012] The term "beverage", as used herein, means a drinkable composition. Beverages include, but are not limited to the following: water, carbonated water, flavored water, carbonated flavored water, milk obtained from animals, milk product derived from soy, rice, coconut or other plant material, sports drinks, vitamin enhanced sports drinks, high electrolyte sports drinks, highly caffeinated high energy drinks, coffee, decaffeinated coffee, tea, tea derived from fruit products, tea derived from herb products, decaffeinated tea, wine, champagne, malt liquor, rum, gin, vodka, other hard liquors, beer, reduced calorie beer-type beverages, non-alcoholic beer, and other beer-type beverages.

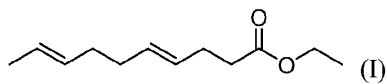
[0013] The term "beer-type beverage", as used herein, means an alcohol-containing or non-alcoholic carbonated beverage having a beer-like flavour. Therefore, the "beer-type beverage" encompasses not only beer, which is a malted fermented beverage obtained by fermenting malt, hops, and water as raw materials using yeast, but also carbonated beverages having a beer flavour. That is, unless otherwise noted, the beer-type beverage of one aspect of the present disclosure may be a fermented beer-type beverage that has undergone a fermentation process using yeast, or may be a non-fermented beer-type beverage that has not undergone a fermentation process. Furthermore, the beer-type beverage of one aspect of the present disclosure may be an alcohol-containing beer-type beverage having an alcohol content of 1 (v / v) % or more, or may be a non-alcoholic beer-type beverage having an alcohol content of less than 1 (v / v) %. It should be noted that the non-alcoholic or alcohol-free beer-type beverage may be a non-alcoholic fermented beer-type beverage produced by removing alcohol produced in a fermentation step after the fermentation step, or may be a non-alcoholic non-fermented beer-type beverage prepared so as to have a beer-like flavour without undergoing a fermentation step, or may be a non-alcoholic or low alcohol beverage produced by a fermentation step using yeast that generates little or no alcohol, or may be a beverage produced by a combination of any of the above methods.

[0014] A common process of producing a non-alcoholic beer-type beverage is described below. With no fermentation step with yeast, a non-alcoholic beer-type beverage can be easily produced. Common non-fermented non-alcoholic beer-type beverages include those produced using malt as a raw material and those not using malt.

5 [0015] In production of non-alcoholic beer-type beverages produced using malt as a raw material, a mixture containing water and raw materials, such as a cereal grain (e.g., a malted grain), and other grains, starch, sugars, bittering agents, or colorants as needed, is mixed with an enzyme such as an amylase as needed. The resulting mixture is gelatinized, saccharified, and filtered to obtain a saccharified solution. The saccharified solution is mixed with hops, a bittering agent, or the like as needed and then boiled, followed by removal of the solids content such as a coagulated protein in a clarification tank. The saccharified solution may be replaced by a boiled mixture of a malt extract, warm water, and hops. Hops may be added to the mixture at any stage from the start of boiling to the end of boiling. The conditions in the saccharification, boiling, solids content removal, and the like may be known conditions. After the boiling, the obtained
10 wort is filtered, and the filtrate is then mixed with carbon dioxide gas. Thereafter, the resulting mixture is packed into a container and sterilized to obtain a desired non-alcoholic beer-type beverage. When decadienoate esters according to the present disclosure are added to this type of non-alcoholic beer-type beverages, the decadienoate esters may be added at any point in the process, for example, after the wort has cooled and either before or after filtration.

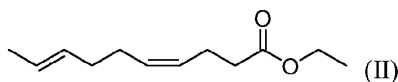
20 [0016] In production of a non-alcoholic beer-type beverage not using malt as a raw material, a liquid sugar containing a carbon source, a nitrogen source as an amino acid-containing material other than a cereal grain or malt, hops, colorants, and the like are mixed together with warm water to obtain a liquid sugar solution. The liquid sugar solution is boiled. When hops are used as a raw material, the hops may be mixed into the liquid sugar solution during boiling, not
25 before the start of boiling. The boiled liquid sugar solution is mixed with a carbon dioxide gas. Thereafter, the resulting mixture is packed into a container and sterilized to obtain a desired non-alcoholic beer-type beverage. When decadienoate esters according to the present disclosure are added to this type of non-alcoholic beer-type beverages, the decadienoate esters may be added at any point in the process, for example, after the wort has cooled and either before or after
30 filtration.

[0017] According to the present disclosure, decadienoate esters according to the following formulas (I, II, III and IV) deliver more authentic hop character and a strong fruity-pear note when used as flavour ingredients in flavour compositions.

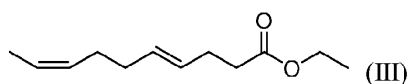


Ethyl (4E,8E) decadienoate

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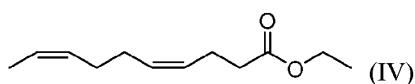


Ethyl (4Z,8E) decadienoate



Ethyl (4E,8Z) decadienoate

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Ethyl (4Z,8Z) decadienoate

15 Thus, according to one embodiment, one or more decadienoate ester compounds may be selected from the group consisting of ethyl (4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z) decadienoate and combinations thereof.

[0018] The flavour compositions according to the present disclosure may have any suitable form, for example liquid or solid, wet or dried, or in encapsulated form bound to or
 20 coated onto carriers/particles, or as a powder. In a typical embodiment, the one or more decadienoate ester compounds present in the flavour composition may be in a concentration of from about 10 ppb to about 100,000 ppm and such flavour compositions would be dosed into a beverage at a range of from about 0.01% to about 1% such that the concentration in the final beverage is from about 0.1 ppb to about 10 ppm.

25 [0019] In another embodiment, the amount in which the one or more decadienoate ester compounds may be added to a consumable may vary within wide limits and depends, inter alia, on the nature of the consumable or additive, on the particular desired effect. It is well within the purview of the person skilled in the art to decide on suitable quantities of the one or more decadienoate ester compounds to incorporate into a consumable depending on the end use and

desired effect. According to certain embodiments, the amount of the one or more decadienoate ester compounds present in the consumable may be in a concentration of from at least about 0.1 ppb to about 10 ppm. According to certain embodiments, the amount of the one or more decadienoate ester compounds in the consumable may be in a concentration of from about 1 ppb to about 100 ppb.

[0020] According to certain embodiments, the amount of the one or more decadienoate ester compounds may be present in a beer-type beverage in a concentration of from about 0.1 ppb to about 100 ppb; in another embodiment of from about 0.1 ppb to about 10 ppb; in another embodiment of from about 1 ppb to about 10 ppb.

[0021] The decadienoate ester compounds according to the present disclosure and formulas (I–IV) can be obtained using straightforward synthetic procedures and readily available starting materials known to a person skilled in the art. In particular, for example, the 4Z isomers can be synthesized utilizing a Wittig reaction between the appropriate 4-hexenal and (4-ethoxy-4-oxobutyl)(triphenyl)phosphonium bromide when potassium tert-butoxide is used as a base. An analogous synthesis is reported by Marcuccio, S. M. et al. WO 01/46115 to synthesize methyl (4Z,8Z)-4,8-decadienoate. The 4E isomers can be synthesized utilizing a Johnson-Claisen rearrangement using an appropriately derivatized allylic alcohol and triethyl orthoacetate.

[0022] Flavour compositions according to the present disclosure may also contain further flavour ingredients. Other further flavour ingredients, besides the decadienoate ester compounds according to the present disclosure and formulas (I–IV), that might be used to provide a flavour composition may be selected from natural flavours, artificial flavours, spices, seasonings, and the like, synthetic flavour oils and flavour aromatics and/or oils, oleoresins, essences, distillates, and extracts derived from plants, leaves, flowers, fruits, and so forth.

[0023] Flavour oils include spearmint oil, cinnamon oil, oil of wintergreen (methyl salicylate), peppermint oil, Japanese mint oil, clove oil, bay oil, hop oil, anise oil, eucalyptus oil, thyme oil, cedar leaf oil, oil of nutmeg, allspice, oil of sage, mace, oil of bitter almonds, and cassia oil; useful flavoring agents include artificial, natural and synthetic fruit flavours such as vanilla, and citrus oils including lemon, orange, lime, grapefruit, yuzu, sudachi, and fruit essences including apple, pear, peach, grape, raspberry, blackberry, gooseberry, blueberry, strawberry, cherry, plum, prune, raisin, cola, guarana, neroli, pineapple, apricot, banana, melon, apricot, cherry, tropical fruit, mango, mangosteen, pomegranate, papaya, and the like, and combinations thereof.

[0024] Additional exemplary flavours imparted by a flavour-producing ingredient may include a milk flavour, a butter flavour, a cheese flavour, a hop flavour, a cream flavour, and a yogurt flavour, a vanilla flavour, tea or coffee flavours, such as a green tea flavour, an oolong tea flavour, a tea flavour, a cocoa flavour, a chocolate flavour, and a coffee flavour; mint flavours, such as a peppermint flavour, a spearmint flavour, and a Japanese mint flavour; spicy flavours, such as an asafetida flavour, an ajowan flavour, an anise flavour, an angelica flavour, a fennel flavour, an allspice flavour, a cinnamon flavour, a chamomile flavour, a mustard flavour, a cardamom flavour, a caraway flavour, a cumin flavour, a clove flavour, a pepper flavour, a coriander flavour, a saffron flavour, a savory flavour, a Zanthoxyli Fructus flavour, a perilla flavour, a juniper berry flavour, a ginger flavour, a star anise flavour, a horseradish flavour, a thyme flavour, a tarragon flavour, a dill flavour, a capsicum flavour, a nutmeg flavour, a basil flavour, a marjoram flavour, a rosemary flavour, a bayleaf flavour, and a wasabi (Japanese horseradish) flavour; a nut flavour such as an almond flavour, a hazelnut flavour, a macadamia nut flavour, a peanut flavour, a pecan flavour, a pistachio flavour, and a walnut flavour; floral flavours; and vegetable flavours, such as an onion flavour, a garlic flavour, a cabbage flavour, a carrot flavour, a celery flavour, mushroom flavour, and a tomato flavour.

[0025] Generally, any flavour-producing ingredient or food additive such as those described in “Chemicals Used in Food Processing”, Publication No 1274, pages 63-258, by the National Academy of Sciences, can be used.

[0026] The consumable may include a product base. As used herein, the term “product base” refers to all the ingredients necessary for the consumable, apart from the one or more decadienoate ester compounds. These will naturally vary in both nature and proportion, depending on the nature and use of the consumable or additive, but they are all well known to the art and may be used in art-recognized proportions. The formulation of such a base for every conceivable purpose is therefore within the ordinary skill of the art.

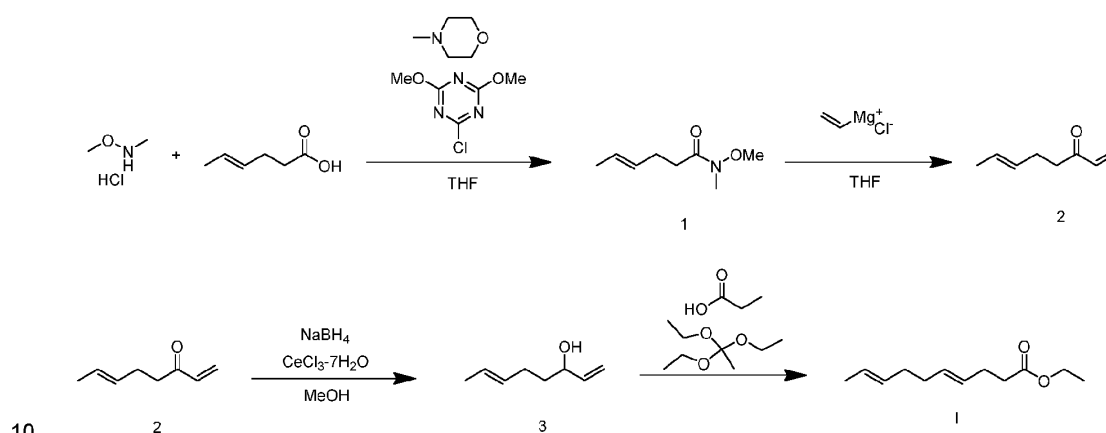
[0027] Without limitation, and only by way of illustration, suitable bases may include, anti-caking agents, anti-foaming agents, anti-oxidants, binders, colourants, diluents, disintegrants, emulsifiers, encapsulating agents or formulations, enzymes, fats, flavour-enhancers, flavouring agents, gums, polysaccharides, preservatives, proteins, solubilisers, solvents, stabilisers, sugar-derivatives, surfactants, sweetening agents, vitamins, waxes, and the like. Solvents which may be used are known to those skilled in the art and include e.g. water, ethanol, ethylene glycol, propylene glycol, glycerine and triacetin. Encapsulants and gums include maltodextrin, gum arabic, alginates, gelatine, modified starch, other polysaccharides, and proteins.

[0028] The disclosure is further described with reference to the following non-limiting examples.

EXAMPLES

[0029] The following examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations of the invention are possible without departing from the spirit and scope of the present disclosure.

Example 1: Synthesis of ethyl (4E,8E) decadienoate (I)



[0030] (E)-N-methoxy-N-methylhex-4-enamide (1):

[0031] (E)-hex-4-enoic acid (4.50 g, 1 Eq., 39.4 mmol) was dissolved in THF (100 mL). Add N-methylmorpholine (12.0 g, 13.0 mL, 3 Eq, 118 mmol) and stir 5 minutes. Add 2-chloro-4,6-dimethoxy-1,3,5-triazine (8.31 g, 1.2 Eq, 47.3 mmol) in 3 portions over 10 minutes. Solution becomes slightly warm and white precipitate forms. Stir at ambient temperature for 90 minutes, then add o,n-dimethyl-hydroxylamine hcl (3.85 g, 1 Eq, 39.4 mmol) in two portions and stir overnight at ambient temperature for 16 hours. Quench reaction with 100 ml of water. Note, not all precipitate goes into solution. Extract aqueous 3 x 50 ml MTBE and combine organics. Wash with saturated potassium bicarbonate solution 2 x 50 ml, 3 X 1 M HCl 50 ml, and brine. Dry over sodium sulfate and remove solvent in vacuo. The desired product was purified by silica gel column chromatography using a hexanes-ethyl acetate gradient. Isolate 2.7 grams 44%) of a clear oil (1).

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[0032] ^1H NMR (300 MHz, CDCl_3) δ = 1.65 (d, J =4.2 Hz, 3H), 2.34 - 2.27 (m, 2H), 2.48 (t, J =7.2 Hz, 2H) 3.18 (s, 3H), 3.68 (s, 3H), 5.54 - 5.41 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ = 17.84, 27.51, 32.15, 61.17, 125.72, 129.94, 174.12.

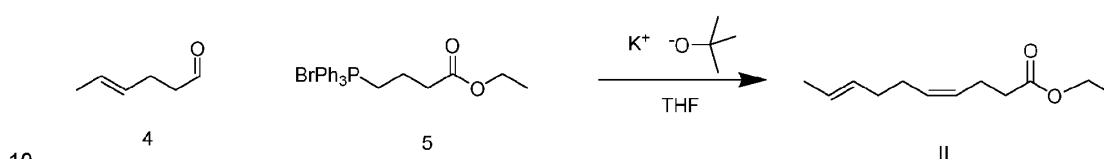
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- [0033] (E)-octa-1,6-dien-3-one (2):
- [0034] (E)-N-methoxy-N-methylhex-4-enamide (2.70 g, 1 Eq, 17.2 mmol) was dissolved in THF (50 mL) and cooled to -20 °C in an isopropyl alcohol / dry ice bath.
- 5 Add Chloro(vinyl)magnesium (1.79 g, 10.3 mL, 2 molar, 1.2 Eq, 20.6 mmol) (purchased from Acros, newly opened bottle) dropwise and stir. Allow reaction to warm to ambient temperature over 1 hour and stir at ambient temperature an additional hour. Cool reaction in ice bath and quench with saturated ammonium chloride. Dilute with water and MTBE. Separate organic layer and extract aqueous 3 X MTBE. Combine organics and wash 1 X brine. Collect organic
- 10 layer and dry over sodium sulfate. Isolate 1.75 grams 82% of clear oil (2).
- [0035] ^1H NMR (300 MHz, CDCl_3) δ = 1.64 (d, J =4.7 Hz, 3H), 2.34 - 2.27 (m, 2H), 2.64 (t, J =7.2 Hz, 2H), 5.53 - 5.37 (m, 2H), 5.82 (dd, J =10.3, 1.3 Hz, 1H), 6.21 (dd, J =17.4, 1.3 Hz, 1H), 6.35 (dd, J =17.4, 10.3, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ = 17.84, 26.84, 39.44, 125.91, 127.96, 129.54, 136.56, 200.3.
- 15 [0036] (E)-octa-1,6-dien-3-ol (3):
- [0037] (E)-octa-1,6-dien-3-one (1.19 g, 1 Eq, 9.58 mmol) dissolved in MeOH (30 mL). Add cerium(III) chloride heptahydrate (3.93 g, 1.1 Eq, 10.5 mmol) and stir at ambient temperature until dissolved. Cool to -5 °C with isopropyl alcohol / dry ice bath. Add sodium borohydride (363 mg, 1 Eq, 9.58 mmol) in three portions and stir for 20 minutes. Quench with
- 20 saturated ammonium chloride solution (100 mL) and extract 5 x 50 mL MTBE. Combine organics and wash with brine. Dry over sodium sulfate and run silica gel column using a pentane-MTBE gradient, Isolate 1.15 g of clear oil (3).
- [0038] ^1H NMR (300 MHz, CDCl_3) δ = 1.66 - 1.54 (m, 5H), 2.11 - 2.04 (m, 2H), 4.14 - 4.08 (m, 1H), 5.10 (d, J =10.5 Hz, 1H), 5.22 (d, J =17.1 Hz, 1H), 5.51 - 5.43 (m, 2H), 5.86 (ddd, J =17.1, 10.5, 6.1, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ = 17.91, 28.48, 36.7, 72.82, 114.57, 125.49, 130.68, 141.13.
- [0039] Ethyl (4E,8E) decadienoate (I):
- [0040] Triethyl orthoacetate (1.25 g, 1.42 mL, 1.95 Eq, 7.73 mmol) and (E)-octa-1,6-dien-3-ol (0.500 g, 1 Eq, 3.96 mmol) and propionic acid (14.7 mg, 14.8 μL , 0.05 Eq, 198 μmol)
- 30 were added to microwave vial, flushed with argon and sealed with a cap. Heat at 100 °C for 2 hours using an oil bath. Then heat to 140 °C for 3 hours. Cool reaction and dilute with a mixture of pentane and MTBE. Wash organic layer 2 x 1 M HCl and 1 x saturated sodium bicarbonate,

and 1 x brine. Dry over sodium sulfate. Run silica gel column using 98:2 pentante-MTBE gradient. Isolate 520 mg of a clear oil (66%).

[0041] ^1H NMR (300 MHz, CDCl_3) δ = 1.25 (t, J =7.1 Hz, 3H), 1.64 - 1.63 (m, 3H), 2.07 - 1.99 (m, 4H), 2.39 - 2.26 (m, 4H), 4.12 (q, J =7.1, 2H), 5.52 - 5.34 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ = 14.26, 17.91, 27.94, 32.53, 32.57, 34.41, 60.23, 125.07, 128.3, 130.77, 131.16, 173.27.

Example 2: Synthesis of ethyl (4Z,8E) decadienoate (II)



[0042] Ethyl (4Z,8E) decadienoate (II):

[0043] Ethyl 4-(bromotriphenyl-15-phosphaneyl)butanoate (4.17 g, 1.2 Eq, 9.11 mmol) was ground into powder and added to 200 ml rb flask and THF (35 mL) was added to the flask. Cool in an ice bath and add potassium *tert*-butoxide (1.02 g, 1.2 Eq, 9.11 mmol) in three portions. Stir for 30 minutes in an ice bath and then for 30 minutes at ambient temperature. Reaction becomes orange in color. Cool reaction again in an ice bath and add a pre-cooled solution of freshly prepared (E)-hex-4-enal (0.745 g, 1 Eq, 7.59 mmol) via canula. Stir reaction for 30 minutes, then ambient temperature for 2.5 hours. Monitor reaction by TLC and GC-MS. Cool reaction in an ice bath and quench with saturated ammonium chloride solution. Dilute with ammonium chloride solution and 50:50 Pentante-MTBE mixture (100 ml). Collect organics and wash with brine. Dry over sodium sulfate. Remove solvent in vacuo. Purify by silica gel column with 50:50 hexanes- CH_2Cl_2 to remove triphenyl phosphine oxide. A second column on isolated material was run using a 99.5 pentante-0.5 MTBE gradient to 98:2 pentante-MTBE. Pure fractions were collected and the solvent removed in vacuo to yield 0.450 grams (30%) of a clear oil (II).

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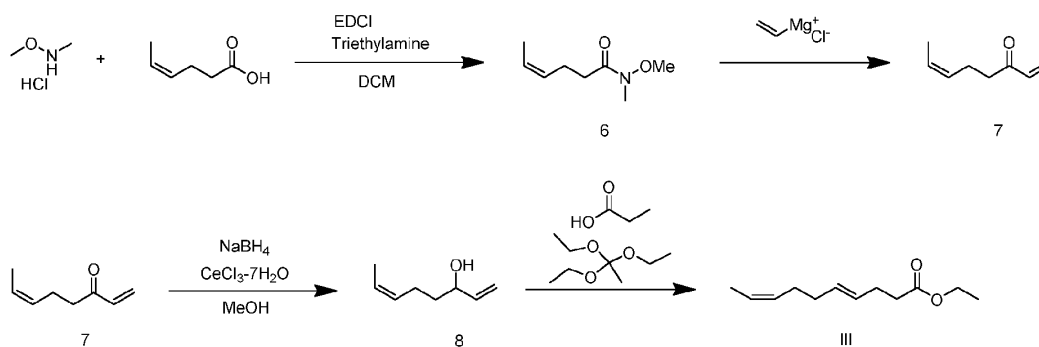
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[0044] ^1H NMR (300 MHz, CDCl_3) δ = 1.25 (t, J =7.1 Hz, 3H), 1.65 - 1.63 (m, 3H), 2.14 - 1.99 (m, 4H), 2.38 - 2.31 (m, 4H), 4.11 (q, J =7.1, 2H), 5.47 - 5.30 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ = 14.25, 17.91, 22.88, 27.27, 32.54, 34.39, 60.3, 125.24, 127.71, 130.76, 173.26.

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Example 3: Synthesis of ethyl (4E,8Z) decadienoate (III)



[0045] (Z)-N-methoxy-N-methylhex-4-enamide (6):

5 [0046] (Z)-hex-4-enoic acid (2.00 g, 1 Eq, 17.5 mmol) was dissolved in DCM (80 mL) and cooled in an ice bath. Add triethylamine (5.32 g, 7.33 mL, 3 Eq, 52.6 mmol) via syringe slowly, followed by o,n-dimethyl-hydroxylamine hcl (1.71 g, 1 Eq, 17.5 mmol) in two portions. Stir for 10 minutes then add 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimideHydrochloride (EDCI) (3.36 g, 1 Eq, 17.5 mmol) in 3 batches over 10 minutes. Stir reaction and allow ice bath
10 to come to room temperature. Stir overnight for 20 hours. Large amount of white precipitate forms. Reaction was diluted with 100 ml of water and partition in separatory funnel. Extract aqueous 3 x 30 ml of DCM. Combine organics and wash 2 x 100 ml 1 M HCl, 2 x saturated sodium bicarbonate 50 ml, and brine 1 x 50 ml. Dry over sodium sulfate. Purify by silica gel column chromatography. Collect 1.6 g (58%) of a clear oil (6).

15 [0047] ¹H NMR (300 MHz, CDCl₃) δ = 1.64 (d, J=6.2 Hz, 3H), 2.41 - 2.34 (m, 2H), 2.51 - 2.48 (m, 2H), 3.18 (s, 3H), 3.68 (s, 3H), 5.54 - 5.36 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ = 12.71, 22.08, 31.79, 61.19, 124.99, 129.03, 174.1.

[0048] (Z)-octa-1,6-dien-3-one (7):

[0049] (Z)-N-methoxy-N-methylhex-4-enamide (1.60 g, 1 Eq, 10.2 mmol) was dissolved
20 in THF (50 mL) and cooled to -20 °C in an isopropyl alcohol / dry ice bath. Add Chloro(vinyl)magnesium (1.06 g, 6.11 mL, 2 molar, 1.2 Eq, 12.2 mmol) (purchased from Acros, newly opened bottle) dropwise and stir. Allow reaction to warm to ambient temperature over 1 hour. Stir an additional 60 minutes. Cool reaction in an ice bath and quench with saturated ammonium chloride. Dilute with water and MTBE. Separate organic layer and wash aqueous 3
25 X MTBE. Combine organics and wash 1 X brine. Collect organic layer and dry over sodium sulfate. Purify by silica gel column. Isolate 647 mg 51% of a clear oil (7).

[0050] ^1H NMR (300 MHz, CDCl_3) δ = 1.63 (d, J =7.2 Hz, 3H), 2.40 - 2.33 (m, 2H), 2.65 (t, J =7.3, 2H), 5.41 - 5.32 (m, 1H), 5.54 - 5.42 (m, 1H), 5.83 (dd, J =10.3, 1.3, 1H), 6.22 (dd, J =17.6, 1.3, 1H), 6.36 (d,d, J =17.6, 10.3, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ = 12.7, 21.4, 39.31, 125.1, 128, 128.67, 136.54, 200.31.

5 [0051] (Z)-octa-1,6-dien-3-ol (8):

[0052] (Z)-octa-1,6-dien-3-one (0.647 g, 1 Eq, 5.21 mmol) was dissolved in MeOH (25 mL). Add cerium(III) chloride heptahydrate (2.14 g, 1.1 Eq, 5.73 mmol) and stir at room temp until dissolved. Cool to -5 C with isopropyl alcohol / dry ice bath. Add sodium borohydride (197 mg, 1 Eq, 5.21 mmol) in three portions and stir for 30 minutes. Quench with saturated ammonium chloride solution (100 ml) and extract 5 x 50 ml MTBE. Combine organics and wash with brine. Dry over sodium sulfate and run silica gel column 95:5 Pentane-MTBE to 90:10 pentane-MTBE. Isolate 0.601 g (91%) of clear oil (8).

[0053] ^1H NMR (300 MHz, CDCl_3) δ = 1.65 - 1.56 (m, 5H), 2.18 - 2.11 (m, 2H), 4.16 - 4.09 (m, 1H), 5.11 (d, J =10.2, 1H), 5.23 (d, J =16.7, 1H), 5.51 - 5.36 (m, 2H), 5.88 (ddd, J =6, 10.2, 16.7). ^{13}C NMR (125 MHz, CDCl_3) δ = 12.78, 22.84, 36.68, 114.68, 124.56, 129.85, 141.12.

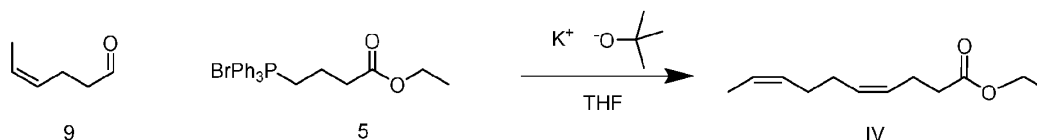
[0054] Ethyl (4E,8Z) decadienoate (III):

[0055] (Z)-octa-1,6-dien-3-ol (0.550 g, 1 Eq, 4.36 mmol) was dissolved in a microwave vial with triethyl orthoacetate (4.95 g, 5.59 mL, 7 Eq, 30.5 mmol) and add propionic acid (12.9 mg, 13.0 μL , 0.04 Eq, 174 μmol). The vial was sealed with a cap and heated to 100 C for 3 hours. Then heat reaction to 140 C for 2.5 hours. The reaction was cooled and diluted with 100 ml of 50:50 pentane-MTBE. Wash organic layer with 2 X 1 M HCl, 1 x saturated sodium bicarbonate solution, and 1 x brine. Collect organics and dry over sodium sulfate. Run silica column to purify using 100% pentane to 98:2 Pentane-MTBE gradient. Isolate 473 mg of III as a clear oil.

[0056] ^1H NMR (300 MHz, CDCl_3) δ = 1.25 (t, J =7.1 Hz, 3H), 1.59 (d, J =5.9, 3H), 2.09 - 2.02 (m, 4H), 2.39 - 2.27 (m, 4H), 4.12 (q, J =7.1, 2H), 5.53 - 5.32 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ = 12.81, 14.27, 26.8, 27.94, 32.4, 34.39, 60.24, 124.09, 128.39, 129.91, 131.13, 173.26.

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Example 4: Synthesis of ethyl (4Z,8Z) decadienoate (IV)



5 [0057] Ethyl (4Z,8Z) decadienoate (IV):

[0058] Ethyl 4-(bromotriphenyl-15-phosphaneyl)butanoate (5.59 g, 1.2 Eq, 12.2 mmol) was ground into powder and added to 200 ml rb flask and THF (40 mL) was added to the flask. Cool reaction in an ice bath and add potassium *tert*-butoxide (1.37 g, 1.2 Eq, 12.2 mmol) over three portions. Stir for 30 minutes in an ice bath and then for 30 minutes at ambient temperature.

10 The reaction becomes orange in color. Cool reaction again in ice bath and add a pre-cooled hexane-DCM solution of (Z)-hex-4-enal (1.00 g, 1 Eq, 10.2 mmol) via canula. Stir in ice bath 30 minutes, then room temperature for 2.5 hours. The reaction was quenched after 4 hours with saturated ammonium chloride solution. Extract aqueous phase 1 x MTBE. Combine organics and wash with brine. Collect organics. Dry over sodium sulfate and remove solvent in vacuo to obtain an oil. Some solids precipitate. Dissolve product in small amount of dichloromethane and dilute to 50:50 mixture with hexane. Purify on silica gel column using 50:50 CH₂Cl₂:Hexane solvent system to remove triphenyl phosphine oxide. A second silica gel column was run using a pentane-MTBE gradient 100% pentane to 98:2 pentane-MTBE. Fractions were cut to obtain 0.9 grams of pure IV as a clear oil.

20 [0059] ¹H NMR (300 MHz, CDCl₃) δ = 1.26 (t, J=7.1, 3H), 1.61 (d, J=5.9, 3H), 2.15 - 2.04 (m, 4H), 2.40 - 2.30 (m, 4H), 4.13 (q, J=7.1, 2H), 5.49 - 5.32 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ = 12.81, 14.26, 22.87, 26.85, 27.14, 34.41, 60.31, 124.31, 127.86, 129.91, 130.77, 173.25.

[0060] Decadienoate ester compounds (I-IV) were then tested in a formulated model beer base and their additional effect on the aroma and taste of the model beer (base + esters) was noted in Table I as compared to control (base without esters).

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Table I

<u>Ingredient</u>	<u>Taste Evaluation (vs control)</u>
0.1 ppb of I	more hoppy
0.1 ppb of II	more hoppy
0.1 ppb of III	more hoppy
0.1 ppb of IV	more hoppy
1.0 ppb of I	hoppy, fruity, waxy, sweaty, honey, fermented hoppy, fruity, waxy, sweaty, honey, fermented
1.0 ppb of II	hoppy, fruity, waxy, sweaty, honey, fermented
1.0 ppb of III	hoppy, fruity, waxy, sweaty, honey, fermented
1.0 ppb of IV	hoppy, fruity, waxy, sweaty, honey, fermented
10 ppb of I	same, stronger, heavy
10 ppb of II	same, stronger, heavy
10 ppb of III	same, stronger, heavy
10 ppb of IV	same, stronger, heavy
100 ppb of I	same, stronger, heavy
100 ppb of II	strong hoppy
100 ppb of III	fruity, strong hoppy
100 ppb of IV	same, stronger, heavy
1 ppm of I	same, stronger, heavy
1 ppm of II	strong fruity, pineapple, metallic
1 ppm of III	fruity, hoppy,
1 ppm of IV	same, stronger, heavy
10 ppm of I	fruity, metallic
10 ppm of II	same, stronger
10 ppm of III	fruity, pineapple, metallic

10 ppm of IV	metallic, fishy
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- [0061] When expressed as “ppm”, the concentration is parts per million by weight based on the total weight of the consumable or additive, as the situation dictates. It should be understood that when a range of values is described in the present disclosure, it is intended that any and every value within the range, including the end points, is to be considered as having been disclosed. For example, “a range of from 1 ppm to 1000 ppm” of roasted barley taste modifying extract is to be read as indicating each and every possible number along the continuum between 1 and 1000. It is to be understood that the inventors appreciate and understand that any and all values within the range are to be considered to have been specified, and that the inventors have possession of the entire range and all the values within the range.
- 10 [0062] In the present disclosure, the term “about” used in connection with a value is inclusive of the stated value and has the meaning dictated by the context. For example, it includes at least the degree of error associated with the measurement of the particular value. One of ordinary skill in the art would understand the term “about” is used herein to mean that an amount of “about” of a recited value produces the desired degree of effectiveness in the compositions and/or methods of the present disclosure. One of ordinary skill in the art would further understand that the metes and bounds of “about” with respect to the value of a percentage, amount or quantity of any component in an embodiment can be determined by varying the value, determining the effectiveness of the compositions or methods for each value, and determining the range of values that produce compositions or methods with the desired degree of effectiveness in accordance with the present disclosure.
- 20 [0063] While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.
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What is claimed is:

1. A flavour composition comprising:
one or more decadienoate ester compounds selected from the group consisting of ethyl
5 (4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z)
decadienoate and combinations thereof; and
one or more further flavour ingredients.
2. The flavour composition according to claim 1, comprising from 10 ppb to 100,000 ppm of
10 the one or more decadienoate ester compounds.
3. The flavour composition according to claim 1 comprising from 100 ppb to 10,000 ppm of
the one or more decadienoate ester compounds.
- 15 4. A consumable comprising the flavour composition of claim 1.
5. The consumable according to claim 4, wherein the consumable is a beverage.
6. The consumable according to claim 5, wherein the beverage is a beer-type beverage.
20
7. A beer-type beverage comprising:
one or more decadienoate ester compounds selected from the group consisting of ethyl
(4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z)
decadienoate and combinations thereof; and
25 a product base.
8. The beverage of claim 7, wherein the beverage has an alcohol content of less than 1.0%.
9. The beverage of claim 8, wherein the beverage is an alcohol-free beer-type beverage.
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10. The beverage of claim 7, wherein the beverage has an alcohol content of greater than
1.0%.

11. The beverage of claim 10, wherein the beverage is an alcohol-containing beer-type beverage.

12. Use of one or more decadienoate ester compounds selected from the group consisting of
5 ethyl (4E,8E) decadienoate, ethyl (4Z,8E) decadienoate, ethyl (4E,8Z) decadienoate, ethyl (4Z,8Z) decadienoate and combinations thereof, as an ingredient to confer, enhance, improve or modify the hops taste of a beer-type beverage.