

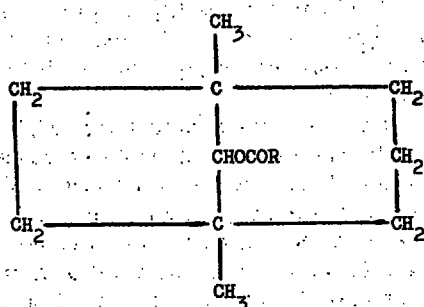
SPECIFICATION

New derivatives of 1,5-dimethylbicyclo[3.2.1]-octane, the preparation of these compounds, and their use as perfume compounds

The invention relates to new derivatives of 1,5-dimethylbicyclo[3.2.1] octane, to their use as perfume compounds, to perfume compositions containing these new compounds, to articles and materials perfumed with the new compounds, and to the preparation of these compounds.

There is a growing interest in the preparation and use of synthetic perfume materials. This interest is stimulated not only by the insufficient availability of natural perfume materials, but also by the fact that, unlike natural products, synthesis perfumes can be produced with constant quality.

Surprisingly, it has now been found that derivatives of 1,5-dimethylbicyclo[3.2.1]octane with the general formula:



wherein R represents hydrogen or an aliphatic group or an aromatic hydrocarbon group optionally substituted with an amino group, are valuable perfume compounds with a strong flowery and/or minty odour with a pleasant woody note. Formula I comprises both compounds with the syn- and with the anti-configuration.

The hydrocarbon group preferably contains one to twenty carbon atoms and may be saturated or unsaturated and branched or unbranched. It may be, for instance, an alkyl, alkenyl, alkynyl, cycloalkyl or aryl group.

The compounds according to the invention may be used as such as fragrance materials but they can also successfully be used in perfume compositions. Preferred perfume compounds are those having the above general formula I, wherein R represents hydrogen or a hydrocarbon group containing one to seven carbon atoms. The hydrocarbon group is preferably an aliphatic hydrocarbon group with from one to seven carbon atoms, in particular with from one to four carbon atoms.

Examples of compounds according to the invention having the general formula I are the formate, acetate, propionate, butyrate, isobutyrate, pivalate, valerate and anthranilate of 1,5-dimethyl-bicyclo[3.2.1]octanol-8.

Higher esters, for example those derived from carboxylic acids containing at least 5 carbon atoms, may also be incorporated in perfume compositions in view of their fixative properties.

The term "perfume composition" as used herein means a mixture comprising fragrance and, optionally, auxiliary components, dissolved in a suitable solvent or mixed with a powdery substrate if desired, and used to impart a desirable odour to the skin and/or to various kinds of products.

Examples of such products are: soaps, detergents, dishwashing and cleansing agents, air fresheners and room deodorants, pomanders, candles, cosmetics, such as creams, ointments, toilet waters, pre- and after-shave lotions, talcum powders, hair care products, body deodorants and anti-perspirants.

Fragrance components are mixtures thereof which can be used in preparing perfume compositions may include natural products like essential oils, absolutes, resinoids, balsams and concretes, but also synthetic fragrance compounds, such as, e.g. hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, and nitriles, which may be saturated or unsaturated aliphatic, carbocyclic or heterocyclic compounds.

Examples of fragrance compounds which can be used in combination with compounds according to the invention are: geraniol, geranyl acetate, linalool, linalyl acetate, tetrahydrolinalool, citronellol, citronellyl acetate, myrcenol, myrcenyl acetate, dihydromyrcenol, dihydromyrcenyl acetate, tetrahydromyrcenol, terpineol, terpinyl acetate, nopol, nopyl acetate, beta-phenylethanol, beta-phenylethyl acetate, benzyl alcohol, benzyl acetate, benzyl salicylate, benzyl benzoate, amyl salicylate, styralyl acetate, dimethylbenzyl carbinol, trichloromethyl-phenyl-carbinyl acetate, p-tert.-butylcyclohexyl acetate, iso-nonyl acetate, vetiveryl acetate, vetiverol, alpha-hexyl cinnamaldehyde, alpha-n-pentyl cinnamaldehyde, 2-methyl-3-(p-tert.-butyl-phenyl)-propanol, 2-methyl-3-(p-isopropylphenyl)-propanol, 3-(p-tert.-butylphenyl)-propanol, tricyclo-dodecenyl acetate, tricyclododecenyl propionate, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene carbaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexene carbaldehyde, 4-acetoxy-3-pentyl-tetrahydropyran, 3-carboxy-methyl-2-pentylcyclopentane, 2-n-heptyl-cyclo-pentanone, 3-methyl-2-pentyl-2-cyclopentanone, 2-hexyl-2-cyclopentenone, n-decanal, n-dodecanal, 9-decanol-1, phenoxyethyl iso-butyrate, phenylacet-aldehyde dimethyl acetal, phenylacetaldehyde diethylacetal, geranyl nitrile, citronellyl nitrile, cedryl acetate, 3-iso-camphyl-cyclohexanol, cedryl methyl ether, isolongifolanone, aubepine nitrile, heliotropine, coumarin,

eugenol, vanillin, diphenyl oxide, hydroxycitronellal, ionones, methyl ionones, isomethyl ionones, irones, cis-3-hexanol and esters thereof, indan-musk fragrances, tetralin musk fragrances, isochroman musk fragrances, macrocyclic ketones, macrolacton musk fragrances, ethylene brassilate, aromatic nitro musk fragrances.

5 Auxiliary components and solvents which may be used for the preparation of perfume compositions containing compounds according to the invention are, e.g., ethanol, isopropanol, diethylene glycol monoethyl ether and diethyl phthalate. 5

The amount of the derivative of 1,5-dimethyl-bicyclo[3.2.1]octane with the general formula I that can be used in a perfume composition or in a product to be perfumed may vary within wide limits and depends, 10 among other factors, on the product to be perfumed, the nature and the amount of the other components of the perfume composition and the overall odour effect sought to be achieved. Therefore, it is only possible to state very rough limits, which will, however, give the expert an idea of the odour strength and the potentialities of the fragrance compounds according to the invention. In most cases an amount as low as 0.01% by weight will be sufficient to impart a slight, but clearly perceptible flowery or minty note to a 15 perfume composition or to a product to be perfumed. In so-called extrait perfumes and in products perfumed with perfume compositions this concentration is, of course, proportionally lower, depending on the amount of perfume composition used in the end product. 15

In view of their high thermal stability esters having the general formula I, particularly those derived from carboxylic acids containing at least five carbon atoms may be of interest as heat transmission fluids, for 20 example transformer oils, brake fluids, oil additives or synthetic lubricants. Since they are difficult to saponify, esters of tertiary alkane carboxylic acids are of particular interest. Suitable tertiary alkane carboxylic acids or mixtures of tertiary alkane carboxylic acids can conveniently be prepared by reacting one or more olefins, for example containing 4 to 20 carbon atoms with carbon monoxide and water in the presence of an acid catalyst (e.g., hydrogen fluoride or sulphuric acid or boron trifluoride/phosphoric acid 25 mixtures). The reaction product so formed contains no primary acids; secondary acids may generally be present herein in a quantity not exceeding 15%. 25

The compounds with the general formula I can be synthesized by various methods known for the preparation of esters. 1,5-dimethylbicyclo[3.2.1]octanol-8 may for instance be reacted with a carboxylic acid RCOOH, wherein R has the above-mentioned meaning, optionally in the presence of a catalyst such as, for 30 instance, sulphuric acid, hydrogen chloride, boron trifluoride or an acid ion exchange resin. Or 1,5-dimethylbicyclo[3.2.1] octanol-8 may be reacted with the acid chloride of the desired carboxylic acid in the presence of a catalyst, such as, e.g., sodium acetate, pyridine or trimethylamine or with the acid anhydride of the carboxylic acid, optionally in the presence of a catalyst, such as sulphuric acid, boron trifluoride or an acid ion exchange resin. 30

35 In many cases the ester can be obtained in high yield by heating 1,5-dimethylbicyclo[3.2.1]octanol-8 with a mixture of a carboxylic acid, such as for instance acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid or pivalic acid and the anhydride or the carboxylic acid concerned, preferably at a temperature between 100°C and 180°C, in the presence of an acidic ion exchange resin, such as for instance the strongly acid macroreticular cation exchange resin "AMBERLYST" 15, which is marketed by BDH Chemicals Ltd. 40 ("AMBERLYST" is a trade mark). It is preferred to use a small excess of the carboxylic acid anhydride, for instance 5% mol. calculated on 1,5-dimethylbicyclo[3.2.1]octanol-8. 40

The compound with the general formula I, wherein R is hydrogen, the formate, may for instance be obtained by heating 1,5-dimethylbicyclo[3.2.1]octanol-8 with formic acid.

1,5-Dimethylbicyclo[3.2.1]octanol-8 and its preparation by reaction of 1,5-dimethyl-1,5-cyclo-octadiene 45 with a solution of HClO_4 in water-dioxane has been described in an article by J.K. Whitesell, R.S. Matthews and P.A. Solomon in Tetrahedron Letters No. 19, pages 1549-1552 (1976). This method gives the desired product in a yield of only 50%. In addition, the use of perchloric acid has disadvantages. However, the compound can be obtained in higher yield by means of a new process which has been described in our co-pending application No. 7916208. This process comprises hydrolysis or alcoholysis, for instance with 50 sodium methylate in methanol, of esters, particularly the formate, of 1,5-dimethylbicyclo[3.2.1]octanol-8 which in turn can be prepared in a very high yield from 1,5-dimethyl-1,5-cyclo-octadiene. 50

By means of the new process compounds with the general formula I can be prepared by reacting 1,5-di-methyl-1,5-cyclo-octadiene, optionally in the presence of an acidic catalyst, with carboxylic acid with the formula RCOOH, wherein R has the above-mentioned meaning. This process is particularly suitable for 55 the preparation of the formate of 1,5-dimethylbicyclo[3.2.1] octanol-8, which can be obtained in high yield by heating 1,5-dimethyl-1,5-cyclo-octadiene with formic acid, preferably at a temperature between 40 and 100°C. It is preferred to use an excess of formic acid, for instance 2 to 10 mol. per mol. of the dimethylcyclo-octadiene. Addition of a catalyst is not necessary. The excess of formic acid may be distilled off after the reaction and the residue be worked up in the usual way, for instance by diluting with a solvent, 60 neutral washing and fractional distillation. Although it is preferred to use formic acid with a water content of from 0 to 10%w, it is possible, if desired, to use formic acid with a higher water content of from 10 to 40%w, in particular when a phase transfer catalyst, such as for instance "ALQUAT" (tri-sec. octylmethylammonium chloride) ("ALQUAT" is a trade mark), is added to the reaction mixture. 60

If according to the new process it is desired to react 1,5-dimethyl-1,5-cyclo-octadiene with the carboxylic 65 acid RCOOH, addition of an acid catalyst to the reaction mixture is generally necessary if the pK value of the 65

carboxylic acid concerned is greater than 4. Suitable catalysts are, e.g., sulphuric acid, phosphoric acid, p-toluenesulphonic acid and in particular acid cation exchange resins, such as for instance "AMBERLYST" 15.

In the new process a suitable starting material is a mixture consisting of 1,5- and 1,6-dimethyl-1,5-cyclo-octadiene, which, as is mentioned in French patent specification 1,283,217 and Netherlands patent application 7800529, can be obtained by dimerization of isoprene. The presence of 1,6-dimethyl-1,5-cyclo-octadiene in the reaction mixture does not interfere with the formation of the desired ester and its separation from the reaction mixture.

Compounds with the general formula I, wherein R represents an aliphatic hydrocarbon group or an aromatic one optionally substituted with an amino group, can also be obtained by using transesterification methods. For instance, an ester of 1,5-dimethylbicyclo[3.2.1]octanol-8 and a lower carboxylic acid RCOOH can be converted into an ester of the said compound and a higher carboxylic acid RCOOH. For instance, transesterification of the formate of 1,5-dimethylbicyclo[3.2.1]octanol-8 may be effected with an ester RCOOR₁, wherein R represents a primary or secondary alkyl group with preferably from 1 to 7 carbon atoms and R₁ a primary alkyl group with preferably from 1 to 3 carbon atoms, in particular a methyl or an ethyl group. The esters, for instance the anthranilate of 1,5-dimethylbicyclo[3.2.1]octanol, can also be obtained by transesterification of 1,5-dimethylbicyclo[3.2.1]octanol-8 with an ester of the desired acid and a primary alcohol with from 1 to 4 carbon atoms, for instance methyl anthranilate, in the presence of a catalyst.

A very convenient catalyst for the transesterification is an alkali or alkaline earth metal alcoholate of 1,5-dimethylbicyclo[3.2.1]octanol-8. The amount of catalyst lies preferably between 1 and 10, in particular between 2 and 6% mol., calculated on the starting ester of 1,5-dimethylbicyclo[3.2.1]octanol-8. If desired, the alcoholate may be prepared *in situ* from the alkali or alkaline earth metal, e.g. sodium and 1,5-dimethylbicyclo[3.2.1]octanol-8, by adding these compounds to the transesterification mixture. On the other hand, the alcoholate may be prepared separately, for instance by heating the alkali metal or the hydride thereof under nitrogen with an excess of 1,5-dimethylbicyclo[3.2.1]octanol-8 at 60-200°C and then distilling off the excess of the latter compound.

EXAMPLE I - Preparation of the formate of 1,5-dimethylbicyclo[3.2.1]octanol-8

An amount of 420 ml (11.46 mol.) 98-100% formic acid was introduced into a round-bottomed flask and with vigorous stirring 430 ml (2.74 mol.) dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) were pumped into the formic acid at a temperature of 60°C over a period of 1.5 hour. The dimethylcyclo-octadiene was completely converted. Then, 90% of the formic acid was distilled off *in vacuo* at 60°C together with a bicyclic olefin, which was isolated by means of extraction with pentane. The residue was taken up in 200 ml pentane and washed with water and an aqueous solution of NaHCO₃. After drying over Na₂SO₄ the pentane was distilled off and the residue fractionally distilled *in vacuo*. The yield of the formate of 1,5-dimethylbicyclo[3.2.1]octanol-8, boiling point 68°C at 133 Pa, was 392 g (2.15 mol.; 97%, calculated on 1,5-dimethyl-1,5-cyclo-octadiene). By means of gas chromatography the purity was shown to be higher than 99%. The product was identified by measuring the infrared- and NMR-spectra. Infrared spectrum: 1000, 1185 and 1730 cm⁻¹. The formate consisted of 92%w syn- and 8%w anti-isomer. Repetition of the experiment with formic acid which contained 10%w water produced the formate in a yield of 94.8%, calculated on 1,5-dimethyl-1,5-cyclo-octadiene. When formic acid with a higher water content (40%w) was used, addition of a phase transfer catalyst was found to be necessary to obtain reasonable yields.

The formate of 1,5-dimethylbicyclo[3.2.1]octanol-8 has a fresh, minty odour with a slight woody note.

EXAMPLE II - Preparation of the acetate of 1,5-dimethylbicyclo[3.2.1]octanol-8

a) Preparation of 1,5-dimethylbicyclo[3.2.1]octanol-8

1) An amount of 182 g of the formate of 1,5-dimethyl-bicyclo[3.2.1]octanol-8 was dissolved in 100 ml methanol and the solution was slowly added to a mixture of 50 g NaOH, 50 ml H₂O and 200 ml methanol. After the exothermic reaction had terminated the reaction mixture was refluxed for 10 minutes. The methanol was distilled off *in vacuo* and pentane was added to the residue. After washing with water and drying over Na₂SO₄, 152 g crystalline 1,5-dimethylbicyclo[3.2.1]octanol-8 were obtained (melting point 43°C) by concentrating and cooling of the pentane solution. The yield was quantitative. The structure was confirmed by measuring the infrared- and NMR-spectra. The weights of syn- and anti-isomer were in the ratio of 92:8.

2) 1,5-Dimethylbicyclo[3.2.1]octanol-8 was also prepared by dissolving 8.8 g of the formate of 1,5-dimethylbicyclo[3.2.1]octanol-8 in 50 ml absolute methanol and adding 10 mg of sodium to the solution. After refluxing for four hours, methanol and formed methyl formate were distilled off and the residue was taken up in pentane. The solution was washed with water and dried over Na₂SO₄. Distilling off the pentane yielded 6 g crystalline product with a purity higher than 98%.

b) Acetylation of 1,5-dimethylbicyclo[3.2.1]octanol-8

An amount of 20 g (0.13 mol.) 1,5-dimethylbicyclo[3.2.1]octanol-8 was dissolved in 25 ml acetic acid and

15 g (0.14 mol.) acetic anhydride and 0.2 g "AMBERLYST" 15 ion exchange resin were added to the solution. After being heated for 5 minutes at 100°C the reaction mixture was filtered and acetic acid and acetic anhydride were distilled off. The residue was dissolved in pentane and the solution washed with water and NaHCO₃ solution. After being dried over Na₂SO₄ the pentane was distilled off and the residue fractionally distilled in vacuo. An amount of 25 g of the acetate of 1,5-dimethylbicyclo[3.2.1]octanol-8 was obtained with a boiling point of 74°C at a pressure of 90 Pa. Infrared spectrum: 1050; 1235 and 1740 cm⁻¹. The weights of the syn- and anti-isomer were in the ratio of 92:8. The acetate has a fresh, flowery odour with a woody note.

EXAMPLE III- Preparation of the acetate of 1,5-di-methylbicyclo[3.2.1]octanol-8 by transesterification of the formate

a) From pure formate

An amount of 20 g (0.11 mol.) of the formate of 1,5-dimethylbicyclo[3.2.1]octanol-8 was dissolved in 60 ml ethyl acetate, and 130 mg Na and 850 mg 1,5-dimethylbicyclo[3.2.1]octanol-8 were added to the solution. The mixture was refluxed for 3 hours after which the sodium had dissolved. It was shown by gas chromatography that 38% of the formate had been converted into the acetate. The flask was now fitted with a Vigreux and ethyl acetate was distilled off over a period of 3.5 h at a temperature of 60°C. During the distillation 30 ml ethyl acetate were added. At the end of the distillation it was shown by gas chromatography that more than 95% of the formate had been converted. Then, 50 ml of pentane were added and the precipitated sodium alcoholate of 1,5-dimethylbicyclo-[3.2.1]octanol-8 filtered off. The filtrate was washed with water and dried over Na₂SO₄. After the pentane had been distilled off the residue was fractionally distilled in vacuo. An amount of 21 g of the desired acetate was obtained with a boiling point of 74°C at a pressure of 80 Pa.

The yield was 97.4% calculated on the formate. The 1,5-dimethylbicyclo[3.2.1]octanol-8 added was quantitatively recovered in the form of the alcoholate.

b) From crude formate

Over a period of 1 hour 68 g of crude dimethyl-1,5-cyclo-octadiene (a mixture of 80% by weight 1,5-dimethyl-1,5-cyclo-octadiene, 14% by weight 1,6-dimethyl-1,5-cyclo-octadiene and 6% by weight limonene) were added with vigorous stirring to 100 g of 98-100% formic acid at a temperature of 60°C. After keeping the mixture 15 minutes at 70°C most of the formic acid was distilled off in vacuo together with a bicyclic olefin originating from the 1,6-dimethyl-1,5-cyclo-octadiene. The remaining formic acid was removed by adding 200 ml of toluene and subsequent azeotropic distillation. After distilling off the toluene, 150 ml of dry ethyl acetate, 3 g of 1,5-dimethylbicyclo[3.2.1]-octanol-8 and 0.5 g of sodium were added to the residue (containing the formate of 1,5-dimethylbicyclo-[3.2.1]octanol-8). The flask was fitted with a Vigreux distillation column and ethyl formate together with a small quantity of ethyl acetate was distilled off over a period of 5 hours at a temperature of 68°C (top). The remaining ethyl acetate was then distilled off, and the residue fractionally distilled in vacuo. An amount of 67.2 g of the acetate of 1,5-dimethyl-bicyclo[3.2.1]octanol-8 having a boiling point of 98°C at a pressure of 2400 Pa was obtained. By means of gas chromatography the purity was shown to be higher than 99%. The limonene which was present in the crude dimethyl-1,5-cyclo-octadiene polymerized in the presence of formic acid to heavy products which did neither interfere with the transesterification reaction nor with the working up of the reaction mixture. The polymers remained in the bottom of the vacuum distillation.

EXAMPLE IV - Preparation of the propionate, butyrate, isobutyrate, pivalate and valerate of 1,5-dimethylbicyclo[3.2.1]octanol-8

These esters were prepared in an analogous way to that described for the acetate in Example IIb. 1,5-Dimethylbicyclo[3.2.1]octanol-8 was dissolved in a mixture of the carboxylic acid concerned and the anhydride thereof. The catalyst was "AMBERLYST" 15, which was added in an amount of 1%w calculated on the amount of dimethylbicyclo-octanol used. In all cases an excess of 5% mol. acid anhydride was used. The reaction mixture was heated at 120-160°C for 20 minutes. The carboxylic acid and the excess of anhydride were then largely distilled off in vacuo. The residue was taken up in pentane and the solution was washed with an 8% KOH solution in a mixture of 75%v water and 25%v methanol. Saponification of the esters formed did not occur here. After being dried over Na₂SO₄ the pentane was distilled off and the residue was fractionally distilled in vacuo. The ester yield was always higher than 99%. Physical constants of the esters prepared in the way indicated above are listed in the following Table:

	Boiling point	Melting point	Infra-red spectrum	
5 Propionate	86°C/40 Pa		1040; 1195; 1215; 1750	5
10 Butyrate	92°C/27 Pa		1030; 1180; 1215; 1740	10
Isobutyrate	88°C/27 Pa		1030; 1170. 1200; 1745	
15 Pivalate	90°C/27 Pa	61°C	1030; 1050; 1160; 1170; 1740	15
20 Valerate	99°C/27 Pa		1040; 1180; 1745	20

- 25 The valerate was also prepared by transesterification of the formate of 1,5-dimethylbicyclo-[3.2.1]octanol-8 with ethyl valerate after addition of 5% mol. of sodium and 5% mol. of 1,5-dimethylbicyclo[3.2.1]octanol-8 using the method described in Example IIIa. The product obtained was identical to that obtained by reacting 1,5-dimethyl-bicyclo[3.2.1]octanol-8 with valeric anhydride in valeric acid.
- 30 The propionate has a fresh, flowery odour with a strong woody note.
The pivalate has a fresh, minty odour with a woody note.
The butyrate has a fresh, flowery and woody odour.
The valerate has a fresh, minty odour with a woody note.

35 EXAMPLE V - Preparation of the acetate of 1,5-dimethylbicyclo[3.2.1]octanol-8 from dimethyl-1,5-cyclo-octadiene 35

- a) An amount of 20.4 g dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) was dissolved in 100 ml acetic acid and, after addition of 2 g "AMBERLYST" 15, boiled under reflux with vigorous stirring. After six hours the conversion was 98%. The reaction mixture was filtered, diluted with water and extracted with pentane. The pentane solution was washed with water and an aqueous NaHCO_3 solution, dried, evaporated and fractionally distilled. The yield of the desired acetate was 53.3%, calculated on 1,5-dimethyl-1,5-cyclo-octadiene. The weights of the syn- and anti-isomer were in the ratio of 85:15.
- 40 b) An amount of 13.6 g (0.1 mol.) dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) was dissolved in 60 ml acetic acid. The solution was cooled to 12°C and 0.5 ml H_2SO_4 was added dropwise with vigorous stirring. During the addition the temperature increased to 39°C. After another two hours at room temperature the conversion of the dimethylcyclo-octadiene was 98% and the reaction mixture was worked up in the way described under a). The yield of the desired acetate was 24%, calculated on 1,5-dimethyl-1,5-cyclo-octadiene. The weights of the syn- and anti-isomer were in the ratio of 85:15.
- 45 50

EXAMPLE VI

- A mixture of 8 g 1,5-dimethylbicyclo[3.2.1]octanol-8, 8 g methyl anthranilate and 60 mg sodium was heated at 140°C for five hours, during which methanol escaped. The removal of the methanol was promoted by applying a slightly sub-atmospheric pressure. Then, water was added and the mixture obtained was extracted with cyclohexane. The extract was washed with 0.1 N H_2SO_4 to remove non-converted methyl anthranilate, and then with an aqueous NaHCO_3 solution. After drying over Na_2SO_4 , the cyclohexane was distilled off and the residue was fractionally distilled in vacuo. An amount of 9.5 g of the anthranilate of 1,5-dimethyl-bicyclo[3.2.1] octanol-8 was obtained with a boiling point of 117°C/40 Pa.
- 55 60

EXAMPLE VII

- A mixture of 50 ml acetic anhydride and 17.2 g of a mixture of tertiary carboxylic acids having 10 carbon atoms per molecule obtained by reacting propylene trimer with carbon monoxide and water in the presence of an acid catalyst was refluxed with vigorous stirring for 3 hours. The excess of acetic anhydride and the acetic acid formed were distilled off. After heating the residue at 180°C for 2 hours remaining amounts of
- 65

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acetic were removed by distillation in vacuo. The residue was heated with stirring at 180°C with 8 g of 1,5-dimethylbicyclo[3.2.1]octanol-8 and 0.5 g of "AMBERLYST" 15 ion exchange resin for 1 hour. The cooled reaction mixture was diluted with cyclo-hexane, filtered and washed with a 8% by weight solution of KOH in a mixture of methanol (80 v) and water (20 v). The solution was dried on Na₂SO₄ and the cyclohexane 5 distilled off. The residue was fractionally distilled giving 12 g of a thick oil with a boiling point of 137-141°C at a pressure of 13.3 Pa. Infrared spectrum: 1030; 1100; 1140; 1260; 1730; 2860 and 2950 cm⁻¹.

EXAMPLE VIII

10	A perfume composition for use in bath foam was prepared according to the recipe given below:	10
	150 pbw terpeneol	
	130 pbw phenylethanol	
	100 pbw benzyl salicylate	
15	70 pbw 4,6,6,7,8,8-hexamethyl-6,7-dihydro-8H-cyclopenta (g) isochroman	15
	60 pbw alpha-hexyl cinnamic aldehyde	
	50 pbw 4-tert.-butyl cyclohexyl acetate	
	50 pbw benzyl acetate	
	50 pbw linalool	
20	40 pbw methyl ionone	20
	40 pbw citronellol	
	40 pbw phenylethyl acetate	
	30 pbw geraniol	
	30 pbw lavender oil	
25	20 pbw anisic aldehyde	25
	10 pbw cedryl acetate	
	10 pbw styrallyl acetate	
	10 pbw benzoin resin Siam	
	10 pbw salbei oil	
30	100 pbw 1,5-dimethylbicyclo[3.2.1]octan-8-yl formate	30
	1000 pbw	

EXAMPLE IX

35	A perfume composition for use in toilet soap was prepared according to the recipe given below:	35
	170 pbw lavender oil Jugoslav	
	100 pbw linalyl acetate	
40	80 pbw bergamot oil	40
	80 pbw dihydromyrcenol	
	70 pbw methanyl acetate	
	50 pbw 4,6,6,7,8,8-hexamethyl-6,7-dihydro-8H-cyclopenta (g) isochroman	
45	50 pbw amyl salicylate	45
	50 pbw linalool	
	50 pbw benzyl salicylate	
	40 pbw rosana NB *	
	40 pbw citronellol	
	30 pbw coumarin	
50	30 pbw cedarwood oil	50
	30 pbw petitgrain oil	
	30 pbw patchouly oil	
	30 pbw benzyl acetate	
	20 pbw musk ketone	
55	50 pbw 1,5-dimethylbicyclo[3.2.1]octan-8-yl acetate	55
	1000 pbw	

* perfume base, marketed by Naarden International N.V.

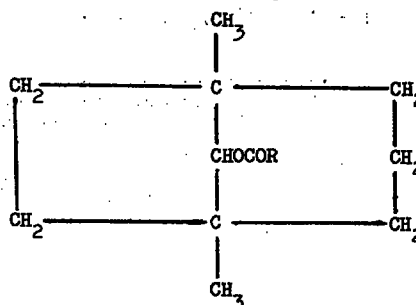


* C L N S *

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C AIMS

1. Derivatives of 1,5-dimethylbicyclo[3.2.1]octane with the general formula:



wherein R represents hydrogen or an aliphatic group or an aromatic hydrocarbon group optionally substituted with an amino group.

2. Derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in claim 1, wherein R is an aliphatic hydrocarbon group with from one to seven, in particular from one to four carbon atoms.

3. Derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in claim 1 or 2, which is the formate, acetate, propionate, butyrate, isobutyrate, pivalate, valerate or anthranilate of 1,5-dimethylbicyclo[3.2.1]octanol-8.

4. Derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in claim 1, which are esters of 1,5-dimethylbicyclo[3.2.1]octanol-8 with a tertiary alkane carboxylic acid or a mixture of tertiary alkane carboxylic acids obtained by reacting one or more olefins with carbon monoxide and water in the presence of an acid catalyst.

5. A process for the preparation of derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in claim 1, wherein 1,5-dimethylbicyclo[3.2.1]octanol-8 is reacted, optionally in the presence of a catalyst, with a carboxylic acid RCOOH, wherein R has the meaning given in claim 1 or 2 or with an acid chloride or acid anhydride of this acid.

6. A process as claimed in claim 5, wherein 1,5-dimethylbicyclo[3.2.1]octanol-8 is reacted with a mixture of the carboxylic acid RCOOH and the anhydride thereof in the presence of an acid ion-exchange resin.

7. A process as claimed in claim 5 or 6, substantially as hereinbefore described with particular reference to any one of the Examples II b, IV and VII.

8. A process for the preparation of derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in claim 1, wherein an ester of 1,5-dimethylbicyclo[3.2.1]octanol-8 and a lower carboxylic acid RCOOH, in which R has the meaning given in claim 1 or 2, is converted by transesterification into an ester of 1,5-dimethylbicyclo[3.2.1]octanol-8 and a higher carboxylic acid RCOOH.

9. A process as claimed in claim 8, wherein the formate of 1,5-dimethylbicyclo[3.2.1]octanol-8 is transesterified with an ester RCOOR₁, where R represents a primary or a secondary alkyl group with from 1 to 7 carbon atoms and R₁ a primary alkyl group with from 1 to 3 carbon atoms.

10. A process as claimed in claim 8 or 9, substantially as hereinbefore described with particular reference to any one of the Examples III and IV.

11. A process for the preparation of derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in claim 1, wherein 1,5-dimethylbicyclo[3.2.1]octanol-8 is transesterified with an ester of the desired acid and a primary alcohol with from 1 to 4 carbon atoms.

12. A process as claimed in any one of claims 8-11, wherein the transesterification is carried out in the presence of an alkali metal alcoholate of 1,5-dimethylbicyclo[3.2.1]octanol-8 as catalyst.

13. A process as claimed in claim 11 or 12, substantially as hereinbefore described with particular reference to Example VI.

14. A process for the preparation of derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in any one of claims 1-4, wherein 1,5-dimethyl-1,5-cyclooctadiene, optionally in the presence of an acid catalyst, is reacted with a carboxylic acid RCOOH, wherein R has the meaning given in claim 1 or 2.

15. A process as claimed in claim 14, wherein 1,5-dimethyl-1,5-cyclo-octadiene is reacted with formic acid at a temperature between 40 and 100°C.

16. A process as claimed in claim 15, wherein 2 to 10 mol. formic acid per mol. of the dimethyl-cyclo-octadiene are used.

17. A process as claimed in claim 15 or 16, wherein formic acid with a water content of from 0 to 10%w is used.

18. A process as claimed in claim 15 or 16, wherein formic acid with a water content of from 10 to 40%w is used in the presence of a phase transfer catalyst.

19. A process as claimed in claim 14, wherein 1,5-dimethyl-1,5-cyclo-octadiene is reacted with a carboxylic acid RCOOH having a pK value greater than 4 in the presence of an acid ion-exchange resin.

20. A process as claimed in any one of the claims 14 to 19, substantially as hereinbefore described with particular reference to any one of the Examples I and V.

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21. Derivatives of 1,5-dimethylbicyclo[3.2.1]octane as claimed in any one of claims 1 to 4, whenever prepared by a process as claimed in any one of claims 5 to 20.
22. Perfume composition, perfumed material or perfumed object containing a derivative of 1,5-dimethylbicyclo[3.2.1]octane as claimed in any one of claims 1 to 4 or 21.

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