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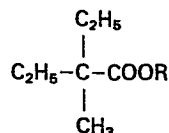
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54 Perfume compositions and perfumed products which contain at least one or more esters of 2-ethyl-2-methyl-butanoic acid as the perfume base.

57 Perfume compositions and perfumed products containing at least one or more esters of 2-ethyl-2-methyl-butanoic acid having the general formula



wherein R represents an alkyl, alkenyl, alkoxyalkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl or aralkyl group having at most 8 carbon atoms.

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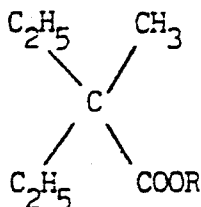
Perfume compositions and perfumed products which contain at least one or more esters of 2-ethyl-2-methyl-butanoic acid as the perfume base.

5 The invention relates to perfume compositions which contain at least one or more esters of 2-ethyl-2-methyl-butanoic acid as the perfume base and to products perfumed with these compounds or with perfume compositions containing these compounds.

10 There is continuing interest in the preparation and use of synthetic fragrances because these, in contrast to natural products, can at all times be prepared in an amount appropriate to demand, and in constant quality.

It has now been found that esters of 2-ethyl-2-methyl-butanoic acid having the general formula

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wherein R represents an alkyl, alkenyl, alkoxyalkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl or aralkyl group having a maximum of 8 carbon atoms are valuable fragrances. They are capable of imparting diverse desired

20 odour notes to perfume compositions and products, namely odour notes of the green, fruity, minty, woody and floral type. The ethyl ester, in particular, is distinguished by a natural odour character. This ethyl ester has been described in British Patent Specification 1,004,286 and

25 by J.R. Roland, J.D.C. Wilson and W.E. Hanford in J. Am. Chem. Soc. 72, 2122-24 (1950). However, in neither publication is there to be found any indication of the usefulness of this compound as a perfume base. As regards the upper limit of 8 carbon atoms, we record, for

30 the sake of completeness, that the volatility and therefore the odour intensity of esters of 2-ethyl-2-methyl-butanoic acid where R contains more than 8 carbon atoms is considered insufficient.

The esters according to the invention are prepared in accordance with generally known esterification methods, for example by reaction of the corresponding alcohol with 2-ethyl-2-methyl-butanoic acid or with a customary derivative thereof, such as the acid chloride.

The esters according to the invention can be used successfully in perfume compositions or are used directly as odour-imparting agents in a variety of products. By the expression "perfume composition", there is here meant a mixture of fragrances and, optionally, auxiliaries, if desired dissolved in a suitable solvent or mixed with a pulverulent substrate, which mixture is used in order to impart a desired odour to the skin and/or to a variety of products. Examples of such products are soaps, detergents, air fresheners, room sprays, pomanders, candles and cosmetics, such as creams, ointments, toilet waters, pre-shave and after-shave lotions, talcum powders, hair-care compositions, body deodorants and antiperspirants.

Fragrances and mixtures thereof which can be used, in combination with the compounds according to the invention, for the preparation of perfume compositions are, for example: natural products such as ethereal oils, absolutes, resinoids, resins, concretes and the like, but also synthetic fragrances such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, nitriles and the like, these including saturated and unsaturated compounds and aliphatic, carbocyclic and heterocyclic compounds. Examples of fragrances which can be used in combination with the compounds according to the invention are geraniol, geranyl acetate, linalool, linalyl acetate, tetrahydrolinalool, citronellol, citronellyl acetate, dihydromyrcenol, dihydromyrcenyl acetate, tetrahydromyrcenol, terpineol, terpinyl acetate, nopol, nopyl acetate, 2-phenylethanol, 2-phenylethyl acetate, benzyl alcohol, benzyl acetate, benzyl salicylate, styrallyl acetate, benzyl benzoate, amyl salicylate, dimethylbenzylcarbinol, trichloromethylphenylcarbinyl acetate, p-tert.-butyl-cyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, alpha-hexylcinnamaldehyde,

2-methyl-3-(p-tert.-butylphenyl)-propanal, 2-methyl-3-(p-isopropylphenyl)-propanal, 3-(p-tert.-butylphenyl)-propanal, tricyclodecanyl acetate, tricyclodecanyl propionate, 4-(4-hydroxy-4-methylpentyl)-cyclohex-3-ene-carbaldehyde, 4-(4-methyl-3-pentenyl)-cyclohex-3-ene-carbaldehyde, 4-acetoxy-3-pentyl-tetrahydropyran, 3-carboxymethyl-2-pentylcyclopentane, 2-n-heptylcyclopentanone, 3-methyl-2-pentyl-2-cyclopentenone, n-decanal, n-dodecanal, dec-9-en-1-ol, phenoxyethyl isobutyrate, phenylacetaldehyde dimethylacetal, phenylacetaldehyde diethylacetal, geranyl nitrile, citronellyl nitrile, cedryl acetate, 3-isocamphyl-cyclohexanol, cedryl methyl ether, isolongifolanone, aubepinenitrile, aubepine, heliotropine, coumarin, eugenol, vanillin, diphenyl oxide, hydroxycitronellal, ionones, methylionones, isomethylionones, irones, cis-hex-3-enol and esters thereof, indane musks, tetralin musks, isochromane musks, macrocyclic ketones, macrolactone musks, ethylene brassylate and aromatic nitro musks.

20 Auxiliaries and solvents which can be used in perfume compositions which contain one or more compounds according to the invention are, for example: ethanol, isopropanol, diethylene glycol monoethyl ether, diethyl phthalate and the like.

25 The quantities in which the compounds according to the invention can be used in perfume compositions or to perfume products can vary within wide limits and depend, inter alia, on the nature of the product wherein the fragrance is used, on the nature and amount of the other components in the perfume composition and on the desired odour effect. Hence, it is only possible to specify very rough limits, but these provide information sufficient for a man skilled in the art to be able independently to use the compounds according to the invention.

30 In most cases an amount of only 0.1% by weight in a perfume composition will already be sufficient to achieve a clearly perceptible odour effect. On the other hand it is possible, in order to achieve special odour effects, to use amounts of 20% by weight or even more in a com-

position. In products perfumed with the aid of perfume' compositions, these concentrations are correspondingly lower, depending on the quantity of perfume composition used in the product.

5 The examples which follow serve solely to illustrate the preparation and use of the compounds according to the invention, but the invention is not restricted thereto.

Example I

10 Preparation of ethyl 2-ethyl-2-methyl-butyrate.

260 g of concentrated sulphuric acid are added in 15 minutes, with efficient stirring, to a mixture of 260 g (2 mol) of 2-ethyl-2-methyl-butanoic acid and 386 g (8 mol) of ethanol. In the course thereof, the
15 temperature rises to about 60°C. The mixture is then heated for 3 hours under reflux, with stirring. When the mixture has cooled to room temperature, the layers are separated.

The lower layer is diluted with 200 ml of water
20 and then extracted with cyclohexane. The cyclohexane layer is combined with the original upper layer and the mixture washed neutral with sodium carbonate solution. The cyclohexane solution is then evaporated and the residue distilled under reduced pressure. 258 g of the
25 desired ethyl ester are obtained, boiling point 65°C/0.3 kPa; $n_D^{20} = 1.4110$; NMR (100 MHz, δ in ppm against TMS, solvent: CCl_4); 0.81 (6H,t,J = 7Hz); 1.06 (3H,s); 1.24 (3H,t,J = 7 Hz); 1.0-1.9 (4H,m); 4.08 (2H,q,J = 7Hz).

The compound has a pleasant fruity and woody
30 odour with aspects which are reminiscent of tagetes oil.

Example II

Preparation of 2'-ethylhexyl 2-ethyl-2-methyl-butyrate.

A mixture of 15.5 g (0.12 mol) of 2-ethylhexanol, 13 g (0.1 mol) of 2-ethyl-2-methyl-butanoic acid, 100 mg
35 of p-toluenesulphonic acid and 150 ml of toluene is heated to the reflux temperature, the water formed being distilled off azeotropically. When the mixture has cooled to room temperature, it is washed neutral with sodium carbonate solution. The toluene solution is then evapo-

rated and the residue distilled under reduced pressure. 14.5 g of the desired ester are obtained, boiling point: 95°C/0.3 kPa; $n_D^{24} = 1.4320$; NMR: 0.81 (6H,t,J = 7Hz); 1.05 (3H,s); 0.6-1.9 (19H,m); 3.90 (2H,d,J = 6Hz).

5 The compound has a pleasant minty and somewhat fruity odour.

Example III

The following esters were prepared as described in Example II:

10 Allyl 2-ethyl-2-methyl-butyrate:

boiling point: 95°C/0.3 kPa; NMR: 0.81 (6H,t,J = 7Hz), 1.08 (3H,s); 1.0-1.9 (4H,m); 4.49 (2H,d with fine structure, J = 7Hz); 5.0-5.4 (2H,m); 5.6-6.1 (1H,m).

15 Spicy green and floral odour, somewhat reminiscent of tagetes oil.

Isobutyl 2-ethyl-2-methyl-butyrate:

boiling point: 90°C/0.3 kPa; $n_D^{20} = 1.4155$; NMR: 0.81 (6H,t,J = 7Hz); 0.94 (6H,d,J = 7Hz); 1.06 (3H,s); 1.0-2.2 (5H,m); 3.78 (2H,d,J = 6Hz).

20 Woody and minty odour with floral tones.

Cyclohexyl 2-ethyl-2-methyl-butyrate:

boiling point: 90°C/0.3 kPa; $n_D^{20} = 1.4462$; NMR: 0.80 (6H,t,J = 7Hz); 1.04 (3H,s); 1.0-2.0 (14H,m); 4.65 (1H,m).

Fruity odour.

25 2'-methoxyethyl 2-ethyl-2-methyl-butyrate:

boiling point: 75°C/0.3 kPa; NMR: 0.81 (6H,t,7Hz); 1.06 (3H,s); 1.0-1.9 (4H,m); 3.30 (3H,s); 3.46 (2H,t,J = 5Hz); 4.12 (2H,t,J = 5Hz).

Green and somewhat woody odour.

30 Benzyl 2-ethyl-2-methyl-butyrate:

boiling point: 118°C/0.3 kPa; $n_D^{20} = 1.4890$; NMR: 0.77 (6H,t,J = 7Hz); 1.07 (3H,s); 1.0-1.9 (4H,m); 5.00 (2H,s); 7.0-7.3 (5H, broad s).

Green and somewhat floral odour.

35 2'-phenylethyl 2-ethyl-2-methyl-butyrate:

boiling point: 125°C/0.3 kPa; $n_D^{20} = 1.4830$; NMR: 0.73 (6H,t,J = 7Hz); 1.01 (3H,s); 1.0-1.9 (4H,m); 2.86 (2H,t,J = 7Hz); 4.20 (2H,t,J = 7Hz); 6.9-7.3 (5H, broad s).

Floral and somewhat fruity odour.

Example IV

A perfume composition of the pine type, very suitable for shampoos and shower and bath foam preparations was prepared in accordance with the following recipe:

- 345 parts by weight of bornyl acetate
- 100 parts by weight of 2-butyl-4,4,6-trimethyl-1,3-dioxane
- 10 50 parts by weight of Siberian pine-needle oil
- 30 parts by weight of 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl-indane
- 30 parts by weight of benzyl acetate .
- 30 parts by weight of orange oil
- 15 30 parts by weight of linalyl acetate
- 20 parts by weight of olibanum resinoid
- 20 parts by weight of tridecanal
- 15 parts by weight of 4-tert.-butylcyclohexyl acetate
- 20 10 parts by weight of coumarin
- 10 parts by weight of terpineol
- 10 parts by weight of terpinyl acetate
- 10 parts by weight of lavandin oil
- 10 parts by weight of n-decanal
- 25 7 parts by weight of Citrovertal NB 104*
- 5 parts by weight of dodecanal
- 5 parts by weight of styrallyl acetate
- 5 parts by weight of 3-isocamphylcyclohexanol
- 3 parts by weight of α -ionone
- 30 2 parts by weight of isoeugenol
- 30 parts by weight of ethyl 2-ethyl-2-methylbutyrate
- 218 parts by weight of dipropylene glycol
- 1000 parts by weight

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Example V

A perfume composition of the floral fantasy type was prepared in accordance with the following recipe:

- 350 parts by weight of lily of the valley base*
- 200 parts by weight of lilac base*

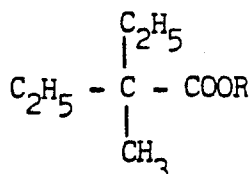
- 175 parts by weight of jasmine base
- 75 parts by weight of hyacinth base *
- 70 parts by weight of rosewood oil
- 70 parts by weight of dihydromyrcenol
- 5 50 parts by weight of ylang-ylang oil
- 40 parts by weight of tricyclodecanyl acetate
- 40 parts by weight of 2-(hept-3-yl)-dioxolane
- 30 parts by weight of litsea-cubeba oil
- 20 parts by weight of dimethyl-benzyl-carbinyl
10 acetate
- 10 parts by weight of eugenol
- 10 parts by weight of 5-acetyl-3-isopropyl-
1,1,2,6-tetramethylindane
- 3 parts by weight of 2,4-dimethyl-cyclohex-
15 3-ene-carbaldehyde
- 2 parts by weight of isoeugenol
- 50 parts by weight of ethyl 2-ethyl-2-methyl-
butyrate
- 1200 parts by weight

20 The perfume compositions as prepared can be used successfully in air freshener preparations produced according to British Patent Specification 1,544,221.

* Perfume bases marked by Naarden International N.V.

CLAIMS

1. Perfume composition or perfumed product, characterised in that it contains one or more esters of 2-ethyl-2-methyl-butanoic acid of the formula



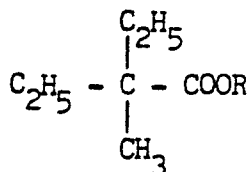
wherein R represents an alkyl, alkenyl, alkoxyalkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl or aralkyl group having at most 8 carbon atoms.

2. Perfume composition or perfumed product according to Claim 1, characterised in that it contains the ethyl ester of 2-ethyl-2-methyl-butanoic acid.

3. Perfume composition according to Claim 1, characterised in that it contains at least 0.1% of one or more of the esters of 2-ethyl-2-methyl-butanoic acid defined in Claim 1.

4. Use of a perfume composition according to one or more of Claims 1-3 or of one or more of the esters of 2-ethyl-2-methyl-butanoic acid defined in Claim 1 for the perfuming of products.

5. Esters of 2-ethyl-2-methyl-butanoic acid of the formula



wherein R represents an alkyl, alkenyl, alkoxyalkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl or aralkyl group having at most 8 carbon atoms, with the proviso that the ethyl ester of 2-ethyl-2-methyl-butanoic acid is excluded.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB-A-1 553 487 (HENKEL) * Page 5, claims 1,4 *	1	C 07 C 69/24 A 61 K 7/46
X	--- CHEMICAL ABSTRACTS, vol. 85, no. 19, November 8, 1976, page 483, no. 142570g, Columbus, Ohio, US; S.D. PIROZHKOV et al.: "Synthesis of allyl esters of neo acids" & ZH. PRIKL. KHIM. (LENINGRAD) 1976, 49(7), 1646-8 * Whole abstract *	5	
X	--- CHEMICAL ABSTRACTS, vol. 80, no. 9, March 4, 1974, page 315, no. 47419k, Columbus, Ohio, US; M.B. ORDYAN et al.: "Hydrocarbalkoxylation reactions. VII. Synthesis of esters from 1-hexene using formic acid and methanol under phosphoric acid catalysis conditions" & ARM. KHIM. ZH. 1973, 26(9), 727-32 * Whole abstract *	5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 69/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-11-1984	Examiner KINZINGER J.M.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			