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[54] **ALKYL DIACETOXY-DIMETHYL-RING SUBSTITUTED-BENZOATES**

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[51] **Int. Cl.²** **C11B 9/00;** C07C 69/78

[58] **Field of Search** ..... 252/522; 260/473 R

[56] **References Cited**

UNITED STATES PATENTS

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Alexander Robertson et al., J. Chem. Soc. London, pp. 3038–3041, 1949.

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[57] **ABSTRACT**

The alkyl diacetoxy-dimethyl-ring substituted-benzoates of this invention have never before been recognized as perfumes or components thereof. They have different and more aggressive odor notes than the corresponding dihydroxy compounds. They may be successfully utilized to imitate or replace the scent of expensive natural oak moss products or odor notes of such products, making then especially useful perfume materials.

7 Claims, No Drawings

ALKYL DIACETO XY-DIMETHYL-RING SUBSTITUTED-BENZOATES

This invention relates to alkyl diacetoxy-dimethyl-ring substituted-benzoates and perfume compositions containing alkyl diacetoxy-dimethyl-ring substituted-benzoates.

In accordance with an aspect of this invention, one or more of certain alkyl diacetoxy-dimethyl-ring substituted-benzoates may be employed in a perfume composition with one or more other odorous perfume components. One or more of the following alkyl diacetoxy-dimethyl-ring substituted-benzoates may be employed for this purpose:

Methyl or ethyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Methyl or ethyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Methyl or ethyl 2,6-diacetoxy-3,5-dimethyl-benzoate
Methyl or ethyl 4,6-diacetoxy-2,3-dimethyl-benzoate

The methyl or ethyl diacetoxy-dimethyl-ring substituted-benzoates of the first six benzoates listed are new compounds. Methyl-4,6-diacetoxy-2,3-dimethyl-benzoate was reported by Alexander Robertson et al. in the *Journal of the Chemical Society* London, 1949, pp. 3038–3041. However, neither this latter benzoate nor any of the other specified benzoates of this invention were disclosed or taught to be of any significance as aroma chemicals in perfumery.

The total amount of the alkyl diacetoxy-dimethyl-ring substituted-benzoate or a mixture of such benzoates is at least 1% by weight, desirably 1 to 30%, and preferably 2 to 5% by weight.

Desirably, the other perfume component or components comprise in their entirety 1 to 99% by weight of the total perfume composition.

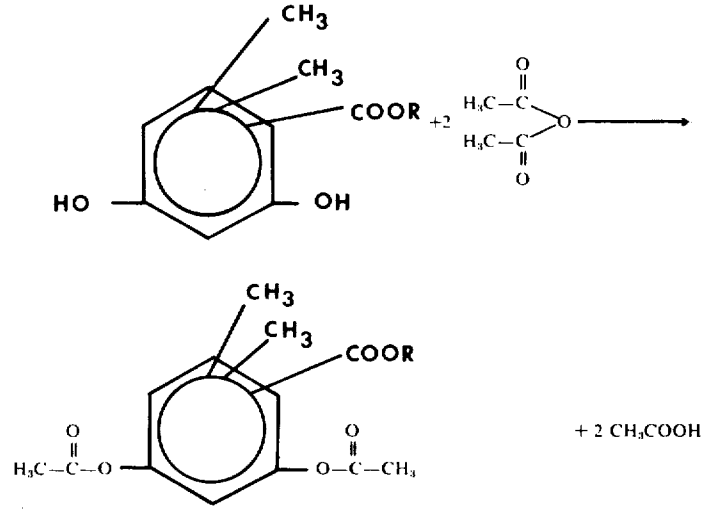
For the production of the perfume compositions of this invention, one or more of the specified alkyl diacetoxy-dimethyl-ring substituted-benzoates are uniformly mixed with one or more of the other perfume components. The specified alkyl diacetoxy-dimethyl-ring substituted-benzoates enhance and/or modify the odors of the perfume compositions. They have significantly aggressive odor notes and are employed to imitate or replace expensive natural oak moss products or odor notes found in such natural products. The alkyl diacetoxy-dimethyl-ring substituted-benzoates employed in the perfume compositions of this invention do not become discolored on standing or when incorporated into perfume compositions or cosmetics, as do other chemicals having one or more phenolic hydroxyl groups in their molecules.

The specified alkyl diacetoxy-dimethyl-ring substituted-benzoates can be used in a variety of different perfume compositions. The compositions may be incorporated in sachet powders, cosmetics such as soaps, creams, body powders and other products such as household products to produce a desired perfume odor.

In accordance with another aspect of this invention, certain of the alkyl diacetoxy-dimethyl-ring substituted-benzoates which are novel compounds may be used in perfumes and for other purposes, such as flavor components. These novel alkyl diacetoxy-dimethyl-ring substituted-benzoates are:

Methyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Ethyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Methyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Ethyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Methyl 2,6-diacetoxy-3,5-dimethyl-benzoate
Ethyl 2,6-diacetoxy-3,5-dimethyl-benzoate

The alkyl diacetoxy-dimethyl-ring substituted-benzoates are produced by reacting acetic anhydride with the required alkyl dihydroxy-dimethyl-ring substituted-benzoate in accordance with the following scheme:



in which R is methyl or ethyl.

The required alkyl dihydroxy-dimethyl-ring substituted-benzoate may be methyl 2,4-dihydroxy-3,6-dimethyl-benzoate, ethyl 2,4-dihydroxy-3,6-dimethyl-benzoate, methyl 2,6-dihydroxy-4,5-dimethyl-benzoate, ethyl 2,6-dihydroxy-4,5-dimethyl-benzoate, methyl 2,6-dihydroxy-3,5-dimethyl-benzoate, ethyl 2,-6-dihydroxy-3,5-dimethyl-benzoate, methyl 4,6-dihydroxy-2,3-dimethyl-benzoate and ethyl 4,6-dihydroxy-2,3-dimethyl-benzoate. The parent chemicals from which the six specified novel alkyl diacetoxy-dimethyl-ring substituted-benzoates are derived are listed in Beilstein's HANDBUCH DER ORGANSCHEN CHEMIE, Vol. 10.

Desirably, a small excess of acetic anhydride is employed, for example, a molecular ratio of 1 mol of the alkyl dihydroxydimethyl-benzoate to 2½ mols of acetic anhydride. Preferably, the reaction is conducted in the presence of a solvent such as xylene which forms an azeotrope with acetic acid.

The formed azeotrope is removed by distillation as it is formed through a fractionation column such as a Vi-

reux column. After completion of the reaction, the ıert solvent and excess anhydride are distilled off in an jector vacuum. If purification is desired, the reaction roduct is dissolved in a suitable inert solvent such as enzene. The resulting solution is washed with water, ɔdium bicarbonate solution, and finally with water. If esired, it is rectified by recrystallization from an apropriate solvent such as isopropanol.

A more comprehensive understanding of this invenon is obtained by reference to the following examples:

EXAMPLE I

Methyl 2,4-Diacetoxy-3,6-dimethyl-benzoate

One mole of methyl 2,4-dihydroxy-3,6-dimethyl-enzoate is combined with 2-1/2 mols of acetic anhyride and 200 ml of xylene. The formed azeotrope conisting of acetic acid and xylene, boiling at 115°–116°C, ; removed as it is formed by distillation through a 1 ft. 'igreux column. After completion of the reaction, the xcess acetic anhydride and xylene are distilled off in n ejector vacuum. The remaining crude reaction prodct is dissolved in 200 ml of benzene. The resulting soıtion is washed successively with water, sodium bicarɔnate solution, and again with water. The methyl 2,4-iacetoxy-3,6-dimethyl-benzoate may be rectified if lesired by recrystallization from a solvent such as isoɔropanol.

If it is desired to produce any of the other alkyl diaceoxy-dimethyl-benzoates utilized in the practice of this nvention, one mol of the required alkyl dihydroxylimethyl-benzoate may be employed instead of the nethyl 2,4-dihydroxy-3,6-dimethyl-benzoate of this exımple. For instance, if ethyl 2,4-diacetoxy-3,6-limethyl-benzoate is desired, it may be obtained by ɛmploying one mol of ethyl 2,4-dihydroxy-3,6-limethyl-benzoate instead of the one mol of methyl 2,-l-dihydroxy-3,6-dimethyl-benzoate and then following he procedure of this example.

EXAMPLE II

Sachet Powder Containing One or More of the Novel Alkyl Diacetoxy-Dimethyl-Ring Substituted-Benzoates as the Only Perfume Component

A sachet powder containing no perfume component ɔther than one or a mixture of two or more of the six ıovel alkyl diacetoxy-dimethyl-ring substituted-ɔenzoates of this invention may be prepared by intinately mixing:

50 parts of one or a mixture of different novel alkyl methyl(or ethyl)diacetoxy-dimethyl-ring substituted-benzoates

50 parts of talcum powder or kaolin or any diatomaceous earth.

In this example, any one or a mixture of the following ıovel alkyl diacetoxy-dimethyl-ring substituted-ɔenzoates may be used totaling 50 parts by weight:

Methyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Ethyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Methyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Ethyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Methyl 2,6-diacetoxy-3,5-dimethyl-benzoate
Ethyl 2,6-diacetoxy-3,5-dimethyl-benzoate

In this example and in all examples which follow, all ɔarts of components and ingredients are by weight.

EXAMPLE III

Musk Sachet Powder

A musk sachet powder is produced by intimately mixing together:

90 parts of one or a mixture of alkyl diacetoxy-dimethyl-ring substituted-benzoates as specified in this example

10 parts of synthetic musk, such as:

Versalide: 1,1,4,4-tetramethyl-6-ethyl-7-acetyl-1,2,3,4-tetrahydronaphthalene; or

Celestolide: 4-acetyl-1,1-dimethyl-6-tert.butylindan; or a nitro-musk such as musk ketone, musk xylene

In this example, any one or a mixture of the following alkyl diacetoxy-dimethyl-ring substituted-benzoates may be used totaling 90 parts by weight of:

Methyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Ethyl 2,4-diacetoxy-3,6-dimethyl-benzoate
Methyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Ethyl 2,6-diacetoxy-4,5-dimethyl-benzoate
Methyl 2,6-diacetoxy-3,5-dimethyl-benzoate
Ethyl 2,6-diacetoxy-3,5-dimethyl-benzoate
Methyl 4,6-diacetoxy-2,3-dimethyl-benzoate
Ethyl 4,6-diacetoxy-2,3-dimethyl-benzoate

EXAMPLE IV

Phantasy Type Perfume Composition

A phantasy type perfume composition is produced by mixing together:

125 parts of one or a mixture of alkyl diacetoxy-dimethyl-ring substituted-benzoates as specified in Example III
300 parts of oil geranium
200 parts of oil ylang ylang
100 parts of heliotropin
100 parts of vanillin
25 parts of iso-eugenol
50 parts of α-amyl-cinnamic aldehyde
50 parts of oil patchouly
30 parts of phenylethyl alcohol
20 parts of orange flowers absolute

EXAMPLE V

New Mown Hay Type Perfume Composition

A new mown hay type perfume composition is produced by mixing together:

20 parts of one or a mixture of alkyl diacetoxy-dimethyl-ring substituted-benzoates as specified in Example III
50 parts of dimethyl hydroquinone
200 parts of oil lavender
250 parts of linalyl acetate
50 parts of methyl salicylate
10 parts of oil clary sage
50 parts of oil ylang ylang
30 parts of tonka bean absolute
10 parts of oil patchouly
5 parts of oil vetivert
50 parts of linalool
10 parts of benzyl acetate
200 parts of hydroxycitronellal
5 parts of diphenyl oxide
30 parts of coumarin
10 parts of vanillin
20 parts of musk ketone

EXAMPLE VI

Fougere Type Perfume Composition

A Fougere type perfume composition is prepared by mixing together:

40 parts of one or a mixture of alkyl diacetoxy-dimethyl-ring substituted-benzoates as specified in Example III
60 parts of linalyl acetate
50 parts of oil lavender
120 parts of oil ylang-ylang bourbon
80 parts of oil geranium
10 parts of oil patchouly
10 parts of oil vetivert
100 parts of vanilla extract
60 parts of α ionone
30 parts of amyl salicylate
5 parts of oil tarragon
150 parts of phenylethyl alcohol
170 parts of α amylcinnamic aldehyde
50 parts of coumarin
30 parts of musk ketone
20 parts of heliotropin

EXAMPLE VII

Chypre Type Perfume Composition

A chypre type perfume composition is prepared by mixing together:

60 parts of one or a mixture of alkyl diacetoxy-dimethyl-ring substituted-benzoates as specified in Example III
30 parts of coumarin
15 parts of oil patchouly
12 parts of oil vetivert
16 parts of oil sandalwood
60 parts of linalkyl acetate
80 parts of oil cedarwood
10 parts of vanillin
20 parts of musk ketone

5 parts of phenylethyl alcohol
7 parts of resinoid labdanum

What is claimed is:

1. A perfume composition comprising at least 1% by weight of an alkyl diacetoxy-dimethyl-ring substituted-benzoate and 1–99% by weight of an odorous perfume component, said alkyl diacetoxy-dimethyl-ring substituted-benzoate being selected from the class consisting of methyl 2,4-diacetoxy-3,6-dimethyl-benzoate, ethyl 2,4-diacetoxy-3,6-dimethyl-benzoate, methyl 2,6-diacetoxy-4,5-dimethyl-benzoate, ethyl 2,6-diacetoxy-4,5-dimethyl-benzoate, methyl 2,6-diacetoxy-3,5-dimethyl-benzoate, ethyl 2,6-diacetoxy-3,5-dimethyl-benzoate, methyl-4,6-diacetoxy-2,3-dimethyl-benzoate and ethyl 4,6-diacetoxy-2,3-dimethyl-benzoate.

2. A perfume composition of claim **1** in which the alkyl diacetoxy-dimethyl-ring substituted-benzoate comprises 1 to 30% by weight of the perfume composition.

3. A perfume composition of claim **1** in which the alkyl diacetoxy-dimethyl-ring substituted-benzoate comprises 2 to 5% by weight of the perfume composition.

4. A perfume composition of claim **1** in which the alkyl diacetoxy-dimethyl-ring substituted-benzoate is methyl (or ethyl) 2,4-diacetoxy-3,6-dimethyl-benzoate.

5. A perfume composition of claim **1** in which the alkyl diacetoxy-dimethyl-ring substituted-benzoate is methyl (or ethyl) 2,6-diacetoxy-4,5-dimethyl-benzoate.

6. A perfume composition of claim **1** in which the alkyl diacetoxy-dimethyl-ring substituted-benzoate is methyl (or ethyl) 2,6-diacetoxy-3,5-dimethyl-benzoate.

7. A perfume composition of claim **1** in which the alkyl diacetoxy-dimethyl-ring substituted-benzoate is methyl (or ethyl) 4,6-diacetoxy-2,3-dimethyl-benzoate.

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