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Kulka et al.

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[45] **May 20, 1975**

[54] **ALKYL MONOMETHYL-RINGSUBSTITUTED-DIACETOXY-BENZOATE PERFUME COMPOSITIONS**

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[52] **U.S. Cl.** ..... **252/522;** 260/473 R

[51] **Int. Cl.** **C11b 9/00**

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

[56] **References Cited**

UNITED STATES PATENTS

3,590,073	6/1971	Carr et al.	260/473 R
3,759,870	9/1973	Economy et al.	260/473 R

Primary Examiner—Veronica O'Keefe

Attorney, Agent, or Firm—Frank M. Nolan

[57] **ABSTRACT**

The alkyl monomethyl-ringsubstituted-diacetoxy-benzoates of this invention have different and more aggressive odor notes than the corresponding dihydroxy compounds. In addition, they do not become discolored on standing or when incorporated into perfume compositions or cosmetics, a common property of chemicals having one or more phenolic hydroxyls. They may be successfully utilized to imitate or replace the scent of expensive natural oak moss products or odor notes of such products, making them novel and useful perfume materials.

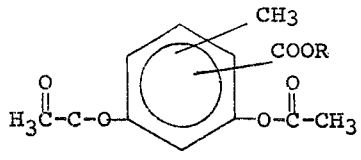
10 Claims, No Drawings

ALKYL MONOMETHYL-RINGSUBSTITUTED-DIACETOXY-BENZOATE PERFUME COMPOSITIONS

This invention relates to alkyl monomethyl-ringsubstituted-diacetoxy-benzoates and perfume compositions containing alkyl monomethyl-ringsubstituted-diacetoxy-benzoates.

In accordance with an aspect of this invention, one or more of the alkyl monomethyl-ringsubstituted-diacetoxy-benzoates may be used with one or more other odoriferous perfume components for the production of a perfume composition. At least 1%, desirably 1 to 30%, and preferably 2 to 5% by weight of one or more of the alkyl monomethyl-ringsubstituted-diacetoxy-benzoates having the following formula is employed:

(1)



in which R throughout the disclosure is methyl or ethyl.

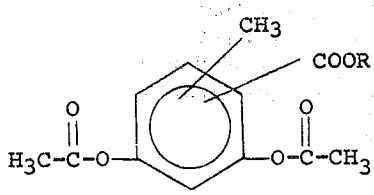
Desirably, the other perfume component or components comprise in their entirety at least 1% by weight of the total perfume composition.

For the production of such perfume compositions, one or more of the alkyl monomethyl-ringsubstituted-diacetoxy-benzoates are uniformly mixed with one or more of the other perfume components. The alkyl monomethyl-ringsubstituted-diacetoxy-benzoates enhance or modify the odors of the perfume composition. They have significant aggressive odor notes and may be utilized to imitate or replace expensive natural oak moss products or odor notes found in such natural products.

The alkyl monomethyl-ringsubstituted-diacetoxy-benzoates are not confined in their application and can be used in a variety of different perfume compositions. Their usage in perfumery is only limited by the skill and imagination of the creative perfumer.

In accordance with another aspect of this invention, certain of the alkyl monomethyl-ringsubstituted-diacetoxy-benzoates which are novel compounds may be utilized per se for perfumes and for other purposes, such as flavors. These novel alkyl monomethyl-ringsubstituted-diacetoxy-benzoates have the formula:

(2)

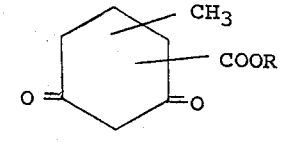


in which R is methyl or ethyl; when the two acetoxy groups are located on the second and fourth carbon atoms of the ring, the methyl group is located on the third carbon atom of the ring; when the two acetoxy groups are located on the third and fifth carbon atoms of the ring, the methyl group is located on the second carbon atom of the ring; when the two acetoxy groups are located on the fourth and sixth carbon atoms of the ring, the methyl group is located on the third carbon atom of the ring; and when the two acetoxy groups are located on the second and sixth carbon atoms of the ring, the methyl group is located on the fourth or fifth carbon atom of the ring.

The alkyl monomethyl-ringsubstituted-diacetoxy-benzoates [(1) or (2)] of this invention may be prepared by esterification of the COOH group of the corresponding monomethyl substituted dihydroxy benzoic acid to the methyl or ethyl ester, followed by acetylation of the two phenolic hydroxy groups.

The alkyl monomethyl-ringsubstituted-diacetoxy-benzoates [(1) or (2)] may also be prepared by a new and novel method of production. This novel method involves the utilization as the starting material of a methyl-carboalkoxy-cyclohexane-dione having the formula:

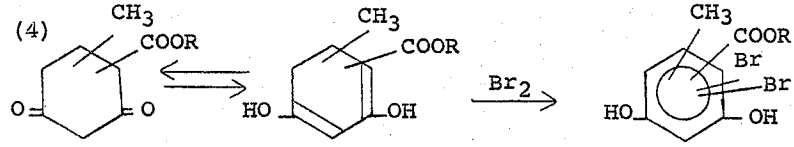
(3)



in which R is methyl or ethyl.

The methyl-carboalkoxy-cyclohexane-dione is first brominated, desirable in the form of a solution such as solution of glacial acetic acid. The reaction which takes place is represented as follows:

(4)

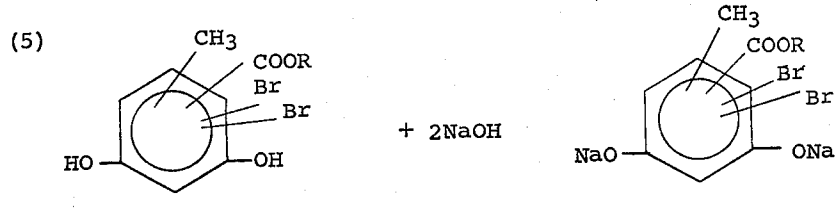


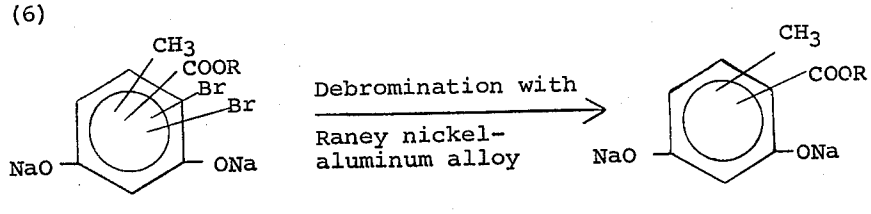
The bromine solution is added slowly to the methyl-carboalkoxy-cyclohexane-dione and its enol with which it is in equilibrium.

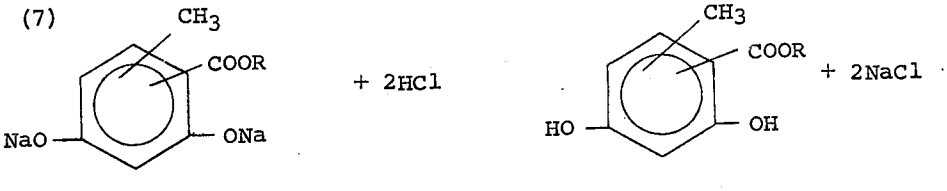
The reaction is desirably conducted over a period of about 4 hours under agitation and cooling, since the reaction is slightly exothermic. Crystals of the resulting alkyl monomethyl-ringsubstituted-dihydroxy-dibromo-benzoate precipitate and are conveniently separated after the addition of water, with cooling. If further purification is desired, the alkyl monomethyl-ringsubstituted-dihydroxy-dibromo-benzoate may be washed once or a plurality of times with a suitable solvent such as water.

The alkyl monomethyl-ringsubstituted-dihydroxy-dibromo-benzoate is debrominated by adding the benzoate, desirably precooled to a temperature of about 0°C, to a dilute alkali metal hydroxide such as sodium or potassium hydroxide. Desirably, the benzoate is added slowly, for example during a period of about 1 hour, to the alkali metal hydroxide solution, which is conveniently an aqueous alkali metal hydroxide solution.

To the resulting solution obtained by the treatment with the alkali metal hydroxide is added slowly, over a period of about an hour, for example, at a temperature of about 0°C, under agitation, Raney nickel-aluminum alloy. After completion of the addition of the alloy, the reaction mixture is allowed to rise to about 5°C and is permitted to stand for a period of about 6 hours at 0°C. The Raney nickel-aluminum alloy is removed from the reaction mixture by any convenient procedure such as filtration. The resulting filtrate solution is cooled to about 0°C and neutralized by any suitable acid, for example a mineral acid, such as concentrated hydrochloric acid. The resulting reaction product is separated. The aqueous part is extract once or a plurality of times with a solvent such as ether. The extract is combined with the reaction product. The resulting solution may be washed once or several times with water. The solvent such as ethyl ether may be removed by distillation from a steam bath. If purification is desired, the resulting debrominated dihydroxy benzoate may be recrystallized from a suitable solvent such as benzene. The reactions which take place are indicated as follows:

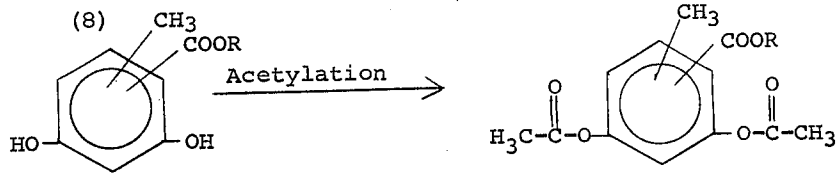






The alkyl monomethyl-ringsubstituted-dihydroxybenzoate is acetylated by mixing it with acetic anhydride, an alkali metal acetate such as sodium acetate and a suitable solvent such as xylene in a distillation flask. The formed azeotrope consisting of xylene and acetic acid is distilled through a Vigreux column. Unreacted acetic anhydride and xylene are removed by distillation from a steam bath under an ejector-vacuum. To the residue is added a quantity of benzene sufficient to effect solution. The resulting solution is washed with water, once or a plurality of times, with an aqueous alkali metal bicarbonate solution such as aqueous sodium bicarbonate solution and finally with water until neutral to litmus. The solvent is removed by distillation from a steam bath under an ejector-vacuum. The crude reaction product, methyl or ethyl methyl-diacetoxybenzoate, may be purified by conventional means such as recrystallization from a solution of suitable solvent or solvents such as a mixture of equal parts of isopropanol and hexane.

The reaction which takes place in the acetylation is as follows:



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

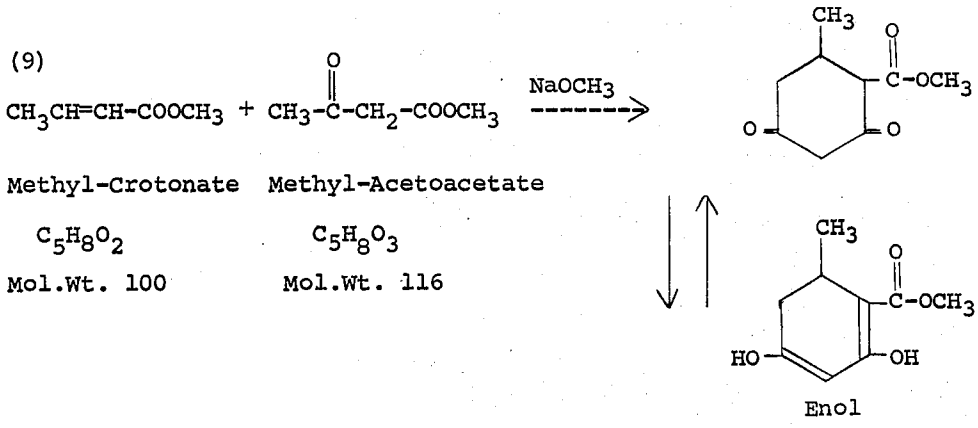
EXAMPLE I

Methyl 6-Methyl-2,4-Diacetoxy-Benzoate

To produce methyl 6-methyl-2,4-diacetoxy-benzoate, 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione is initially produced.

The 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione may be prepared by reacting 1,900 g of methyl crotonate, 2,204 g of methyl acetoacetate, 437 g of sodium and 6,440 ml of methanol in accordance with the following reaction scheme:

(9)

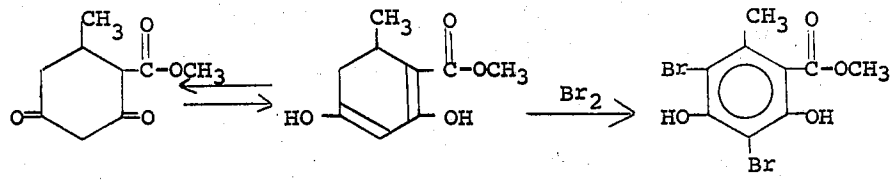


The sodium and methanol are conveniently added in the form of sodium methylate solution, which is prepared by adding gradually the 437 g of sodium to the 6,440 ml of methanol over a period of about 2 hours. The 2,204 g of methyl acetoacetate are added under agitation over a period of 15 minutes to the sodium methylate solution at room temperature. The reaction is exothermic and the temperature rises about 12°C. The reaction mixture is allowed to remain at about room temperature for about an hour after which the 1,900 g of methyl crotonate are added under agitation over a period of about 30 minutes. The resulting reaction mixture is warmed up gradually over a period of about one-half hour to a temperature of about 70°C. The reaction mixture is then refluxed with continued agitation. After approximately 30 minutes from commencement of the refluxing, the reaction becomes vigorous and heat and agitation are discontinued for about 15 minutes. After about 3 hours of reflux under agitation, the reaction mixture becomes cloudy (crystal formation). Agitation and refluxing are continued for an additional 1 hour, and the reaction mixture is then allowed to stand for several hours, such as for overnight at room temperature. The methanol is distilled off at atmospheric pressure during a period of about 5 hours and the removal of methanol is then completed under ejector-vacuum for a period of about an hour. The reaction mass is cooled to about 23°C and the formed crystals are filtered off on a Buchner funnel. The crystals obtained are dissolved in about 3,800 ml of cold water under agitation. The resulting aqueous solution is placed in an ice water bath and 2,500 ml of a 20% sulfuric acid solution (pre-cooled to −20°C) are gradually added under agitation over a period of 45 minutes, while maintaining the temperature of the reaction mass at 20°–22°C.

Upon the addition of the sulfuric acid, crystals are formed. After completion of the addition, agitation is continued for approximately 15 minutes. The crystals are collected on a centrifuge and washed twice with 300 ml of cold water. The crystals are centrifuged to dryness. The white crystals of 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione which are air dried have a melting point of 120°–122.5°C.

The 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione is brominated to produce methyl 6-methyl-2,4-dihydroxy-3,5-dibromo-benzoate in accordance with the following reaction scheme:

(10)



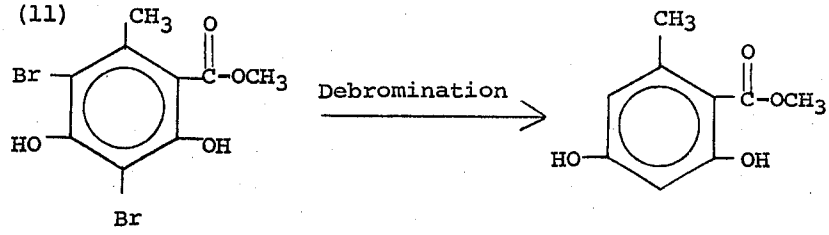
For this purpose, 368 g (2 mols) of 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione and 1,384 ml of glacial acetic acid are combined and heated under agitation to 50°C. A clear solution results. The solution is cooled to 20°C.

The 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione and its enol may be prepared by the process of Adolf Sonn. (b.Vol.61 pp. 926–927, 1928, and Schilling and Vorlander A. Vol. 308, p. 195, 1899).

A solution of 949 g of bromine dissolved in 1,582 g of glacial acetic acid is added under agitation and cooling over a period of 4 hours, the temperature being kept between 20°–25°C to the above prepared solution of 368 g of 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione in 1,384 ml of glacial acetic acid. The solution is permitted to stand for a period of several hours, such as overnight. Crystals precipitate. There is added with agitation and cooling over a period of 45 minutes about 1,500 ml of cold water, the temperature being maintained between 20°–25°C. The crystals of methyl 2,4-dihydroxy-3,5-dibromo-benzoate are centrifuged, washed four times with 250 ml of water, and dried. Analysis shows a bromine content of 45.8% compared with a theoretical of 46.8%.

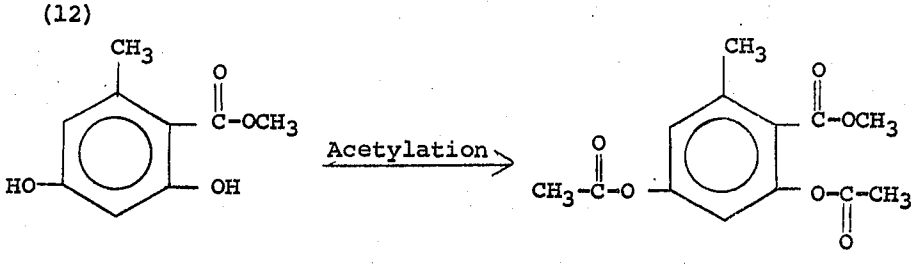
The methyl 6-methyl-2,4-dihydroxy-3,5-dibromo-benzoate is debrominated with Raney nickel-aluminum

alloy to obtain methyl 6-methyl-2,4-dihydroxy-benzoate in accordance with the following reaction scheme:



To produce the debrominated compound, 540 g of methyl 6-methyl-2,4-dihydroxy-3,5-dibromo-benzoate are added over a period of 1 hour to 11,050 ml of a sodium hydroxide solution (pre-cooled to −2°C) prepared by dissolving 885 g of sodium hydroxide in 11,050 ml of water. There are added over a period of 1 hour to the resulting solution, maintained at a temperature of −2°C, with agitation, 473 g of Raney nickel-aluminum alloy (50/50%-Harshaw). After completion of the addition of the Raney nickel-aluminum alloy, the reaction mixture is allowed to rise to 5°C and is maintained at that temperature by cooling since the reaction is slightly exothermic. The reaction mixture is agitated at 4°–5°C for a period of about 6 hours. It is then permitted to stand at 0°C for a period of several hours such as overnight. The nickel catalyst is removed from the reaction mixture by filtration on a Buchner funnel. The filtrate is refiltered to remove traces of the catalyst. The filtrate is then cooled to 0°C and neutralized by the addition of concentrated hydrochloric acid to liberate the methyl 6-methyl-2,4-dihydroxy-benzoate. At the end of the neutralization, the temperature rises to 15°C. The aqueous solution is extracted twice with 500 ml of ethyl ether. The ether extract is combined with the main reaction product and the resulting solution is washed 4 times with 300 ml of water. The ethyl ether is removed by distillation from a steam bath. The resulting crystals are recrystallized from benzene. The crystals are washed with hexane and dried. The dried crystals, methyl 6-methyl-2,4-dihydroxy-benzoate, have a melting point of 140°–143°C. GLC gives one peak.

The methyl 6-methyl-2,4-dihydroxy-benzoate is acetylated in accordance with the following reaction:



$C_{13}H_{14}O_6$

Mol.Wt. 266

To 136.5 g (0.75 mol) of methyl 6-methyl-2,4-dihydroxy-benzoate in a distillation flask are mixed 306 g (3 mols) of acetic anhydride, 563 ml of xylene and 7.5 g of sodium acetate (catalyst). The formed azeotrope consisting of 27.5% xylene and 72.5% acetic acid is distilled through a 14 inches Vigreux column. The azeotrope distillate is about 310 ml. The temperature of the flask is 125°–136°C and the temperature of the vapor is 117°–124°C.

Unreacted acetic anhydride and xylene are removed by distillation from a steam bath under an ejector-vacuum. The residue is dissolved in 350 ml of benzene. The resulting solution is washed successively with 250 ml of water, twice with 50 ml of sodium bicarbonate solution and twice with 50 ml of water. The washed benzene solution is neutral to litmus. The solvent is removed by distillation from a steam bath under an ejector-vacuum. The residue of the crude reaction product is recrystallized from a solution of 170 ml of isopropanol and 170 ml of hexane. The recrystallized methyl 6-methyl-2,4-diacetoxy-benzoate has a melting point of 56°–58°C. The yield is about 80% of the theoretical.

If any of the isomers of methyl 6-methyl-2,4-diacetoxy-benzoate is desired, the same procedure as described in this example is practiced except that instead of employing 2 mols of 5-methyl-6-carbomethoxy-cyclohexane-1,3-dione, 2 mols of the appropriate methyl-carbomethoxy-cyclohexane-dione is substituted therefor.

EXAMPLE II

Methyl 3-Methyl-2,4-Diacetoxy-Benzoate

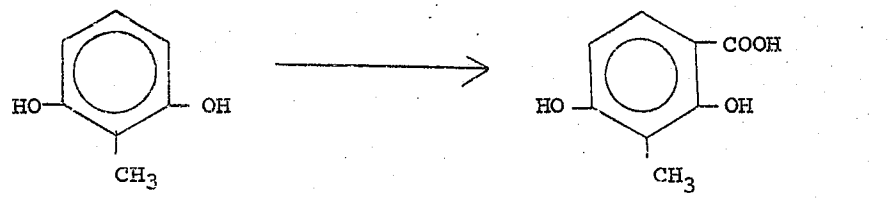
In this method of the preparation of the methyl 3-methyl-2,4-diacetoxy-benzoate, the 1-methyl-2,6-dihydroxy-benzene is utilized as the starting material. The carboxy group is first introduced into the 1-methyl-2,6 -dihydroxy-benzene to produce 3-methyl-2,4-dihydroxy-benzoic acid. The 3-methyl-2,4-dihydroxy-benzoic acid is esterified to produce the methyl or ethyl ester of that benzoic acid. The 2 hydroxy groups of the ester are acetylated to produce the methyl 3-methyl-2,4-diacetoxy-benzoate.

To produce the 3-methyl-2,4-dihydroxy-benzoic

acid, 124 g (1 mol) of 2-methyl-resorcinol, 693 g (8.25 mols) of sodium bicarbonate and 1,710 ml of water are added to a 3-necked reaction flask fitted with thermometer, agitator, reflux condenser and gas delivery tube. The mixture is agitated and heated on a steam bath for 2 hours at a temperature of about 95°C. The 2-methyl-resorcinol and sodium bicarbonate go into solution. A vigorous stream of carbon dioxide is passed into the solution with the gas delivery tube reaching to the bottom of the flask for a period of 2⅓ hours. During the addition of the carbon dioxide, the mixture is agitated and heated to a temperature of between 101°–103°C. After the passage of the carbon dioxide through the solution the hot reaction mixture is neutralized immediately by adding gradually 725 ml of concentrated hydrochloric acid for a period of about 1½ hours, the concentrated hydrochloric acid being added through the gas delivery tube. The temperature at the start of the hydrochloric acid addition is about 101°C, while the temperature at the completion of the hydrochloric acid addition is about 70°C. The reaction mixture is permitted to stand for several hours, such as overnight, at room temperature. The reaction mixture is agitated and cooled to 10°C. It is filtered on a Buchner funnel. The resulting light-colored crystals of 3-methyl-2,4-dihydroxy-benzoic acid having a melting point of 205°–206°C are obtained in a yield of about 64.4%.

The reaction which takes place is indicated as follows:

(13)



1-methyl-2,6-dihydroxy-benzene (2-methyl resorcinol)

3-methyl-2,4-dihydroxy-benzoic acid (3-methyl-beta resorcylic acid)

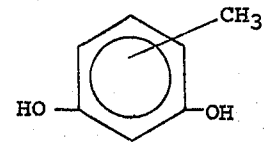
The crystals of 3-methyl-2,4-dihydroxy-benzoic acid which are obtained on the Buchner funnel may be used as such without purification for the next step of esterification.

To produce the methyl ester of 3-methyl-2,4-dihydroxy-benzoic acid, 75 g (0.447 mol) of 3-methyl-2,4-dihydroxy-benzoic acid which is obtained as described and 800 ml of acetone are placed in a 3-necked reaction flask fitted with thermometer, agitator, reflux condenser and dropping funnel. The mixture is agitated until completely dissolved. After a clear solution is observed, 62.5 g (0.743 mol) of sodium bicarbonate are added in one portion to the mixture which is then agitated and heated to reflux to the formation of a light slurry. To this mixture is added over a period of 2 hours 93.6 g (0.743 mol) of dimethyl sulfate with agitation and reflux (temperature 55°–58°C). After the addition of dimethyl sulfate is completed, reflux is continued under agitation for a period of 1½ hours. The mixture is cooled to room temperature and filtered on a Buchner funnel. The acetone is removed by distillation from a steam bath under ejector vacuum. The residue is dissolved in 300 ml of benzene. The benzene solution is washed successively with 100 ml of 5% sodium bicarbonate solution and three times with 300 ml of water. The benzene in the solution is removed by distillation. The methyl 3-methyl-2,4-dihydroxy-benzoate is crystallized from 100 ml of benzene. The crystals are then air dried. The yield is about 81.3% and the ester has a melting point of 125°–128°C.

The methyl 3-methyl-2,4-dihydroxy-benzoate is converted to the methyl 3-methyl-2,4-diacetoxy-benzoate by adding to a 12 liter three-necked flask fitted with thermometer, agitator and a set-up for distillation, 637 g (3.5 mols) of methyl 3-methyl-2,4-dihydroxy-benzoate, 1,430 g (14 mols) of acetic anhydride, 2,600 ml of xylene and 35 g of sodium acetate as a catalyst. The reaction mixture is first refluxed for 2 hours under slow agitation and then the azeotrope of acetic acid-xylene, boiling at 115.4°C at 760 mm, consisting of 72.5 parts of acetic acid and 27.5 parts of xylene, is removed as it is formed by distillation over a period of 12 hours. The distillation is terminated when the flask temperature reaches 130°C and the vapor temperature 124°C. The excess acetic anhydride and xylene is then removed by distillation from a steam bath in an ejector vacuum. The crude reaction mixture is dissolved in 1,000 ml of benzene and washed successively twice with 500 ml of 5% aqueous sodium carbonate solution (slightly basic to litmus) and twice with 500 ml of warm water (neutral to litmus). The solvent benzene is removed by distillation from a steam bath under an ejector vacuum. The reaction product is recrystallized from a solution of 700 ml. of isopropanol and 700 ml of hexane. The crystals are collected on a Buchner funnel, washed with 200 ml of cold hexane and air dried. A yield of about 71.4% of the theoretical is obtained. The melting point of the methyl 3-methyl-2,4-diacetoxy-benzoate is 60°–61°C. V. P. C. analysis as well as wet analysis indicates that a pure product is obtained.

Isomers of the methyl 3-methyl-2,4-diacetoxy-benzoate may be produced by following the procedure of this example except that instead of using 1-methyl-2,6-dihydroxy-benzene as in this example, the appropriate methyl-dihydroxy-benzene having the following generic formula is employed:

(14)



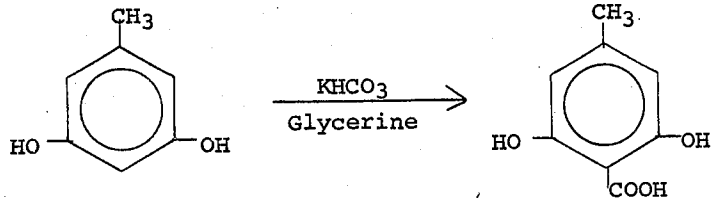
EXAMPLE III

Methyl 4-Methyl-2,6-Dihydroxy-Benzoate

The initial step of the production of the methyl 4-methyl-2,6-dihydroxy-benzoate involves the production of the corresponding benzoic acid. In this initial step, 60 g of orcinol monohydroate, 120 g of potassium bicarbonate and 120 g of glycerine are mixed together and agitated in a nitrogen atmosphere until solution results. Under agitation, the mixture is heated to 115°–120°C for 5½ hours in a nitrogen atmosphere. The mixture is cooled. 150 ml of water are added and the mixture agitated until the solution results. The solution is then neutralized by gradual addition of concentrated hydrochloric acid, keeping the temperature of the reaction mixture below 30°C. The solution is extracted twice with 150 ml of ethyl ether. The resulting ether extract is washed twice with 100 ml of water. The ethyl ether is removed by distillation from a steam bath at atmospheric pressure. The crude reaction product is recrystallized from 190 ml of water.

The reaction which takes place is as follows:

(15)



Orcinol (Monohydrate)

4-Methyl-2,6-Dihydroxy-Benzoic Acid

The 4-methyl-2,6-dihydroxy-benzoic acid has a melting point of 173°C. The yield is about 49.8% of the theoretical.

The methyl ester of 4-methyl-2,6-dihydroxy-benzoic acid is produced by mixing together 30.2 g of 4-methyl-2,4-dihydroxy-benzoic acid, 17.1 g of sodium bicarbonate and 219 ml of acetone and heating the mixture under agitation to reflux at a temperature of 57°–58°C. To the mixture are added over a period of 2 hours 25.6 g of dimethyl sulfate with continued agitation and reflux for an additional 2 hours. The acetone in removed by distillation under agitation. The residue is extracted twice with 50 ml of ethyl ether. The ethyl ether is stripped off by distillation on a steam bath. The crude reaction product is recrystallized with 20 ml of benzene. The yield of methyl 4-methyl-2,6-dihydroxy-benzoate is about 75% of the theoretical. The methyl 4-methyl-2,6-dihydroxy-benzoate has a melting point of 99°–100°C. The V.P.C. gives one peak.

The methyl 4-methyl-2,6-diacetoxy-benzoate is prepared by mixing in a set-up for distillation 18.2 g of methyl 4-methyl-2,6-dihydroxy-benzoate, 40.7 g of acetic anhydride, 75 ml of xylene and 1 g of sodium acetate. The formed acetic acid-xylene azeotrope is removed by distillation through a 6 inch Vigreux column at atmospheric pressure. The azeotrope consists of 27.5% xylene and 72.5% acetic acid. The time of distillation requires about 2½ hours. Boiling point of the azeotropic mixture is 119°–126°C. The excess acetic acid and xylene is then removed by distillation in an ejector vacuum. The residue of the crude reaction product is dissolved in 75 ml of benzene and washed successively with a 5% sodium bicarbonate solution and twice with 50 ml of water. The solvent is removed by distillation from a steam bath in an ejector vacuum. The product is recrystallized from a mixture of 15 ml hexane and 15 ml of isopropanol. The yield is 88.5% of the theoretical. The methyl 4-methyl-2,6-diacetoxy-benzoate has a melting point of 73°–75°C. The G. L. C. indicates a 99 % purity.

EXAMPLE IV

Ethyl 3-Methyl-2,4-Diacetoxy-Benzoate

To prepare ethyl 3-methyl-2,4-diacetoxy-benzoate, the ethyl ester of 3-methyl-2,4-diacetoxy-benzoic acid is first prepared. For this purpose, 301 g of 3-methyl-2,4-dihydroxy-benzoic acid, 227 g of dry sodium bicarbonate and 3,000 ml of dry acetone are mixed in a flask and heated to reflux under agitation. To the agitating refluxing mixture over a period of 2 hours are added 416 g of diethyl sulfate. The mixture is filtered on a Buchner funnel. A liquid and a solid portion result. The solid portion is washed twice with 200 ml of benzene and the benzene extract is added to the liquid portion. The combined liquid portions are then washed twice with 100 ml of warm water. The solvent is removed by distillation and the resulting residue is recrystallized from a solution of 200 ml of benzene and 50 ml of hexane. The resulting crystals of ethyl 3-methyl-2,4-dihydroxy-benzoate have a melting point of 134°–137°C. The yield of about 74.4% of the theoretical.

The ethyl 3-methyl-2,4-diacetoxy-benzoate is produced from the ethyl 3-methyl-2,4-dihydroxy-benzoate by mixing together 40 g of ethyl 3-methyl-2,4-dihydroxy-benzoate, 105 g of acetic anhydride, 170 g of xylene and 2 g of sodium acetate. The mixture is set up for distillation for removing the formed acetic acid-xylene azeotrope through a 12 inch Vigreux column over a period of approximately 4 hours. The vapor temperature is 116°–125°C. The distillate is 150 ml. After completion of the reaction, the excess acetic anhydride and xylene is removed by distillation from a steam bath under an ejector vacuum. The crude reaction product is taken up in 100 ml benzene and the resulting solution is washed with 2 × 200 ml water, 50 ml of 5% aqueous sodium bicarbonate solution and again 50 ml of water. The solvent is removed from a steam bath under an ejector vacuum. The residue comprises ethyl 3-methyl-2,4-dihydroxy-benzoate and is recrystallized from a mixture of hexane and isopropanol. The melting point of the resulting crystals is 77°–79°C; purity by V. P. C. 99%. The yield is 82.3% of the theoretical.

Other ethyl methyl-diacetoxy-benzoates may be produced by using the appropriate methyl-dihydroxy-benzoic acid and diethyl sulfate, following the procedure in this Example.

The corresponding ethyl methyl-diacetoxy-benzoates may also be produced by following the procedures described in Examples I, II and III by using the corre-

sponding ethyl ester of methyl-dihydroxy-benzoic acid. To produce the corresponding ethyl ester, sodium ethylate ethanol solution is employed instead of sodium methylate methanol solution. In Example I, sodium ethylate ethanol solution may be prepared by gradually adding 437 g of sodium to about 9,200 ml of ethanol over a period of about 2 hours.

EXAMPLE V

Perfume Compositions

The following specific examples show the usefulness of the alkyl monomethyl-ringsubstituted-diacetoxy-benzoates of Formula I in perfumery:

Chypre Type Perfume Base

Parts by Weight
- 50 Methyl(or ethyl) monomethyl-ringsubstituted-diacetoxy-benzoate
- 25 Musk Ambrette
- 10 Musk Ketone
- 600 Linalyl Acetate
- 110 Phenylethyl Alcohol
- 75 Coumarin
- 10 Vanillin
- 10 Oil Orange

Fougere Type Perfume Base

- 180 Oil Lvaenger
- 60 Linalyl Acetate
- 40 Oil Patchouly
- 70 Oil Vetivert Java
- 150 Coumarin
- 75 Amyl Cinnamic Aldehyde
- 40 Oil Neroli
- 33 Sclareol
- 60 Methyl (or ethyl) monomethyl-ringsubstituted-diacetoxy-benzoate

Phanthasy Type Perfume Base

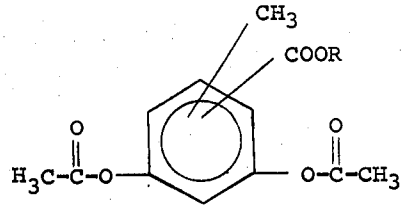
Parts by Weight
- 25 Methyl (or ethyl) monomethyl-ringsubstituted-diacetoxy-benzoate
- 300 Oil Geranium
- 200 Oil Ylang Ylang
- 100 Heliotropin
- 100 Vanillin
- 25 Iso-Eugenol
- 50 α Amyl-Cinnamic Aldehyde
- 50 Oil Patchouly
- 30 Phenylethyl Alcohol
- 20 Orange Flowers Absolute

New Mown Hay Type Perfume Base

- 20 Methyl(or ethyl)monomethyl-ringsubstituted-diacetoxy-benzoate
- 50 Dimethyl Hydroquinone
- 200 Oil Lavender
- 250 Linalyl Acetate
- 50 Methyl Salicylate
- 10 Oil Clary Sage
- 50 Oil Ylang Ylang
- 30 Tonka Beans Absolute
- 10 Oil Patchouly
- 5 Oil Vetivert
- 50 Linalool
- 10 Benzyl Acetate
- 200 Hydroxycitronellal
- 5 Diphenyl Oxide
- 30 Coumarin
- 10 Vanillin
- 20 Musk Ketone

What is claimed is:

1. A perfume composition comprising at least 1% by weight of an alkyl monomethyl-ringsubstituted-diacetoxy-benzoate and at least 1% by weight of an odoriferous perfume component, said alkyl monomethyl-ringsubstituted-diacetoxy-benzoate having the formula:



in which R is methyl or ethyl.

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

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

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

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

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

7. A perfume composition of claim **1** in which the alkyl monomethyl-ringsubstituted-diacetoxy-benzoate is methyl(or ethyl) 5-methyl-2,6-diacetoxy-benzoate.

8. A perfume composition of claim **1** in which the alkyl monomethyl-ringsubstituted-diacetoxy-benzoate is methyl(or ethyl) 2-methyl-3,5-diacetoxy-benzoate.

9. A perfume composition of claim **1** in which the alkyl monomethyl-ringsubstituted-diacetoxy-benzoate is methyl(or ethyl) 4-methyl-3,5-diacetoxy-benzoate.

10. A perfume composition of claim **1** in which the alkyl monomethyl-ringsubstituted-diacetoxy-benzoate is methyl(or ethyl) 3-methyl-4,6-diacetoxy-benzoate.

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