252-99 CROSS REFERENCE EXAMINER

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3,423,430

2-ALKYL SUBSTITUTED-4-METHYL-1,3-DIOXANES

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U.S. Cl. 260—340.7 1 Claim

Int. Cl. C07d *15/04*

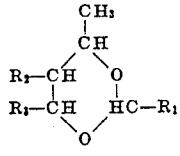
This is a divisional application of Ser. No. 221,318, filed Sept. 4, 1962, now U.S. Patent 3,326,746.

This invention relates to a perfume. More particularly, it relates to a cleaning product with this perfume therein.

It is known that natural geranium oil may be used as a perfume. However, the natural oil is a complicated mixture of numerous components and it has not been possible, heretofore, to form a synthetic product with a suitable geranium note. Even blends prepared by combining the known components of the natural oil do not have the proper odor characteristics.

It is also known to incorporate a perfume into a cleaning product, e.g., a dishwasher product. If, however, the cleaning product contains a chlorine-releasing agent, the prior art perfumes are not satisfactory since they do not overcome the pungent odor resulting from the use of this product. For example, an unsaturated perfume may lose its odoriferous properties and stability because the unsaturation is attacked by the chlorine-releasing agent.

It has now been discovered that a synthetic perfume may be prepared which has a satisfactory geranium-rose note. Furthermore, this perfume may be advantageously employed in cleaning products including those products having chlorine-releasing agents therein. Such a perfume has the following generic structure:



wherein R_1 is an alkyl group having 4 to 9 carbon atoms; R_2 is selected from the group consisting of hydrogen and a C_1 to C_4 alkyl group; and R_3 is selected from the group consisting of hydrogen and methyl.

It is important for the success of the present invention to have a 1,3-dioxane with alkyl groups in at least the 2,4 positions. If R_1 were the only alkyl group, such as isobutyl or 1-ethylpropyl, the compounds therefrom would be devoid of any geranium-rose note. The number of carbon atoms in R_1 is also important; there must be at least 4 carbon atoms but not more than 9 carbon atoms in a straight or branched chain. For example, if R_1 were isopropyl or decyl, the resulting compound would not possess the required geranium-rose note.

Another important feature lies in the 4-methyl substituent in the above structure. The desired perfume would not be provided if higher alkyls, such as ethyl and isopropyl, were employed. Each of the ring carbons must have at least one hydrogen thereon. If a gem-dialkyl group is located on any of the ring carbons, the compounds therefrom do not have a geranium-rose note.

The 2,4-dialkyl-1,3-dioxanes of the present invention may be prepared in accordance with similar procedures known in the art for forming other 1,3-dioxanes. Generally about 1 to 1.5 equivalents of a 1,3-diol are reacted with about 1 equivalent of an aldehyde in the presence of, firstly, a solvent which azeotropes with water, e.g.,

chloroform, ethylene dichloride and benzene, and, secondly, about 0.01% to about 10% of an acid catalyst, e.g., sulfuric acid, hydrochloric acid, p-toluenesulfonic acid and an insoluble resin acid of the sulfonic acid type. The temperature of the reaction is not critical but it is generally maintained between about 40° and 150° C., preferably between about 60° and 100° C.; time varies inversely from about 1 to 6 hours. Water is removed until the reaction is complete with subsequent cooling; neutralization with aqueous alkali, dry alkali, sodium carbonate or the like; washing; and distillation to provide the desired dioxane.

With respect to a second embodiment of this invention, the 2,4-dialkyl-1,3-dioxanes having the geranium-rose note may be incorporated into a cleaning product, e.g., a dishwasher formulation, to overcome the strong odor resulting from the chlorine-releasing compounds therein. The other ingredients usually included in the instant cleaning products besides the dioxanes and chlorine-releasing agents are soaps or non-soap detergents and phosphates. A cleaning product is broadly defined herein as a substance or a composition which removes undesirable dirt, food particles, stains or the like or which renders an item unsoiled. This, therefore, includes dishwashing compounds, dry bleaches, scouring cleansers, light-duty detergents, heavy-duty detergents, pelleted detergents, soap products and scouring pads.

The perfume content depends upon the specific dioxane and the type of cleaning product. Generally, the dioxane perfume is employed in an amount up to about 0.5 part, preferably between about .05 to .25 part, per 100 parts by weight of the total cleaning product (phep.).

Any chlorine-releasing agent known in the art may be satisfactorily utilized in this invention. A chlorine-releasing agent is defined herein as a chlorine-containing compound which liberates chlorine under conditions normally used for cleaning purposes. These agents may range from 0.5 to 40 parts (phep.). Examples of suitable chlorine-releasing agents are as follows. chlorocyanurates, chlorinated trisodium phosphate, N-chlorosuccinimide, calcium hypochlorite, and N,N-dichloroazocarbonamidine.

Soaps and nonsoap detergents, which are usually found in the cleaning products of this invention, are well defined terms of art [Chemistry of Organic Compounds, Noller (1951), pp. 186–90; College Chemistry, Smith (1947), pp. 431–2 and 455]. Any known soap or nonsoap detergent is applicable including the following compounds: sodium lauryl sulfate, sodium alkyldiphenyloxide, alkali metal salts of fatty acids and the wetting agents disclosed in U.S. Pat. No. 2,263,948 which is incorporated herein by reference. These soaps or detergents may comprise about 0.5 to 80 parts (phep.).

The instant cleaning products generally have an alkali metal phosphate therein. This terminology covers a well known class of compounds employed in cleaning compositions (U.S. Pat. No. 2,310,475). The orthophosphates, pyrophosphates, polyphosphates and metaphosphates are applicable to the present invention. These phosphates, e.g., sodium tripolyphosphate, may comprise about 1 to 80 parts (phep.).

A soil-suspending agent, e.g., sodium carboxymethylcellulose and polyvinyl alcohol, is advantageously added in certain types of products within the range of about 0.2 to 1.0 parts (phep.). The following ingredients are also frequently employed: other perfume compounds in combination with the dioxane perfumes; abrasives, e.g., silica; metallic strands (for scouring pads); silicates; carbonates; and borates.

The preferred ranges for the various ingredients in different products are indicated in Table I.

TABLE I

	Preferred range, percent [1]			
	In dishwashing compositions	In dry bleach	In heavy duty detergents	In scouring cleansers
Soaps or nonsoap detergents:				
Sodium lauryl sulfate	1–2	2–4	10–20	2–3
Pluronic L–61 [2]	3–4	2–4	8–10	4–5
Pluronic L–62 [3]	3–4	2–4	8–10	4–5
Sodium alkyldiphenyloxide sulfonate	0.6–0.8	2–4	8–10	4–5
Soap	3–4	2–4	40–80	4–5
Soil-suspending agents:				
Sodium carboxymethylcellulose			0.3–0.5	
Sodium carboxymethyl hydroxy ethyl cellulose			0.3–0.5	
Sodium cellulose sulfate			0.3–0.5	
Polyvinyl alcohol			0.3–0.5	
Polyethylene glycols			0.3–0.5	
Chlorine-releasing agents:				
Trichlorocyanuric acid	8–10	8–10	4–8	8–10
Sodium and potassium dichlorocyanurate	14–16	14–16	5–10	14–16
Dichlorodimethylhydantion	14–16	14–16	5–10	14–16
N-chlorosuccinimide	14–16	14–16	5–10	14–16
Trichloromelamine	14–16	14–16	5–10	14–16
Calcium hypochlorite	14–16	14–16	4–8	14–16
Chlorinated trisodium phosphate	8–10	8–10	4–8	8–10
Chloramine-T [4]	14–16	14–16	5–10	14–16
N,N-dichloro-azocarbonamidine	14–16	14–16	5–10	14–16
Phosphates:				
Sodium tripolyphosphate	40–50	5–20	40–50	5–10
Sodium pyrophosphate	40–50	5–20	40–50	5–10
Sodium hexametaphosphate	40–50	5–20	40–50	5–10
Sodium tetraphosphate	40–50	5–20	40–50	5–10
Sodium trimetaphosphate (soluble)	40–50	5–20	40–50	5–10
Abrasives:				
Silica				85–95
Volcanic ash				85–95
Diatomaceous earth				85–95
Pumice				85–95
Alumina				85–95
Feldspar				85–95
Carborundum				85–95
Fine metallic particles [5]				
Metallic strands [5]				
Plastic web [5]				
Other:				
Sodium metasilicate	10–15	4–8	4–8	1–3
RU-silicate [6]	10–15	4–8	4–8	1–3
N-silicate [7]	10–15	4–8	4–8	1–3
G-silicate [8]	10–15	4–8	4–8	1–3
Sodium carbonate	5–10	5–10	5–15	3–10
Sodium tetraborate	5–10	5–10	5–15	3–10
Sodium sesquicarbonate	5–10	5–10	5–15	3–10
Sodium sulfate (to 100%)				

[1] Percentages are based upon cleaning compound before dioxane perfumes are added thereto.

[2] Empirical formula $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$ wherein b is selected to provide a mol. wt. of propylene oxide of 1,750 and $a+c$ is an integer to provide 10% etnylene oxide in the molecule.

[3] Empirical formula $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$ wherein b is selected to provide a mol. wt. of propylene oxide of 1,750 and $a+c$ is an integer to provide 20% ethylene oxide in the molecule.

[4] Sodium derivative of N-chloro-p-toluene sulfonamide.

[5] Used in scouring pads.

[6] Sodium silicate solution; $SiO_2:Na_2O=2.4:1$.

[7] Sodium silicate solution; $SiO_2:Na_2O=3.25:1$.

[8] 85% sodium silicate solids; $SiO_2:Na_2=3.22:1$.

The dioxanes heretofore described may also be utilized to perfume cleaning compositions without any chlorine-releasing agents therein. These compositions include liquid detergent formulations, soaps and toiletry products, especially those that are neutral or alkaline. Furthermore, a bleaching-type product may be formed which contains only a dioxane perfume and a chlorine-releasing agent.

Thus, in accordance with this invention, a synthetic perfume with a suitable geranium-rose note has been provided. Furthermore, it is now possible to manufacture a cleaning product comprising a chlorine-releasing agent and a 1,3-dioxane perfume which can be used without the formation of an objectionable odor.

The following examples are submitted to illustrate but not to limit this invention. Unless otherwise indicated, all parts and percentages in the specification are based on weight.

EXAMPLE 1

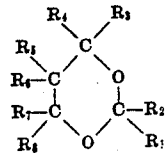
The following compounds were mixed in a 250 ml. flask: 11.4 g. (0.1 mole) of heptaldehyde; 9.9 g. (0.11 mole) of butane-1,3-diol; 150 ml. of benzene; and 0.25 g. of p-toluenesulfonic acid. A reaction was performed at a temperature of 80–85° C. with the water formed therefrom being separated by means of a Dean-Stark trap on the flask. After 3½ hours of refluxing, no further water was formed. The reaction mixture was then cooled to room temperature, neutralized with aqueous sodium carbonate and washed with water until neutral.

Subsequent distillation provided 2-hexyl-4-methyl-1,3-dioxane which had a geranium-rose note. This dioxane was capable of being used to perfume a dishwasher composition with a chlorine-releasing compound therein.

EXAMPLE 2

The compounds indicated in Table II were prepared in accordance with similar procedures as described in Example 1.

TABLE II



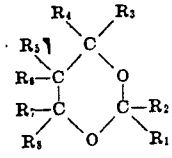
Compounds	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
1	H	n-Butyl	H	CH_3	H	H	H	H
2	H	1-ethylpropyl	H	CH_3	H	H	H	H
3	H	1-methylbutyl	H	CH_3	H	H	H	H
4	H	2-ethylamyl	H	CH_3	H	H	H	H
5	H	n-Heptyl	H	CH_3	H	H	H	H
6	H	n-Octyl	H	CH_3	H	H	H	H
7	H	Isobutyl	H	CH_3	CH_3	H	H	H
8	H	do	H	CH_3	H	H	CH_3	H
9	H	do	H	CH_3	CH_3	H	CH_3	H
10	H	do	H					

All of the above compounds possessed a geranium-rose note and were suitable for incorporation into a product containing a soap or non-soap detergent and a chlorine-releasing agent.

EXAMPLE 3

The compounds listed in Table III were prepared but they did not exhibit a geranium-rose note.

TABLE III



Compounds	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
1	H	Isobutyl	H	H	H	H	H	H
2	H	1-Ethylpropyl	H	H	H	H	H	H
3	H	Isopropyl	H	CH_3	H	H	H	H
4	H	Decyl	H	CH_3	H	H	H	H
5	H	Isobutyl	H	Ethyl	H	H	H	H
6	H	do	H	Isopropyl	H	H	H	H
7	H	do	H	H	CH_3	CH_3	H	H
8	H	do	H	Isopropyl	CH_3	CH_3	H	H
9	H	do	CH_3	CH_3	H	H	CH_3	H
10	H	n-Hexyl	CH_3	CH_3	H	H	CH_3	H
11	H	n-Heptyl	CH_3	CH_3	H	H	CH_3	H
12	H	n-Butyl	CH_3	CH_3	H	H	CH_3	H
13	H	Isobutyl	H	CH_3	CH_3	CH_3	H	H

This example demonstrates the criticality of the substituents on the 1,3 dioxanes in order to provide the desired odoriferous properties.

EXAMPLE 4

Dry chlorinated bleaches were formed with the following ingredients therein.

Ingredient	Parts		
	A	B	C
2-isobutyl-4-methyl-1,3-dioxane	0.10		
2-n-heptyl-4-methyl-1,3-dioxane		0.10	
2-isobutyl-4,6-dimethyl-1,3-dioxane			0.10
Sodium fatty alcohol sulfate	2.1		2.1
Potassium dichlorotriazinetrione	16.7	16.7	
Sodium tripolyphosphate	36.2	36.2	36.2
Sodium silicate	0.4	0.4	0.4
Sodium sulfate	44.4	44.4	44.4
Sodium alkylbenzenesulfonate [1]		2.1	
Halane [2]			16.7

[1] Primarily a 1:1 mixture of alkylbenzene sulfonates in which the alkyl portion is a polypropylene group and has an average of 12 and 15 carbon atoms respectively.
[2] Dichlorodimethylhydantoin.

These bleaches were stored for six days at 95° F. in both closed jars and commercial packages, and the perfume odor was not affected by the chlorine-releasing agents therein.

EXAMPLE 5

A dishwasher product was provided with 0.1% 2-isobutyl-4,5,6-trimethyl-1,3-dioxane and the ingredients shown herebelow.

Ingredient:	Parts
Sodium tripolyphosphate [1]	44.00
Chlorinated trisodium phosphate [1]	9.60
N-Silicate [1]	7.414
RU-Silicate [1]	5.878
Pluronic L62	2.25
Pluronic L61	0.75
Colorants	0.004
Water	30.104

[1] Expressed on dry basis.

After storage for six days at 95° F. in both closed jars and commercial packages, this formulation lost none of its perfume odor.

EXAMPLE 6

The following liquid detergent formulation was per-

fumed with 0.1% of 2-(2-ethyl-propyl)-4-methyl-1,3-dioxane.

Composition:	Percent
Potassium dodecylbenzenesulfonate	10
Sodium xylenesulfonate	8
LDA [2]	2.7
LIPA [3]	3.0
Potassium pyrophosphate	18.0
Sodium silicate	2.5
CMC [4]	0.15
Methocel [5]	0.57
Water (to 100%).	

[2] Lauric/myristic diethanol amide.
[3] Lauric/myristic isopropanol amide.
[4] Sodium carboxymethylcellulose.
[5] Methylcellulose.

The perfume odor of this formulation was unaffected after being stored in accordance with the procedure described in Example 4.

EXAMPLE 7

The scouring cleanser-type formulation indicated herebelow was perfumed with 0.1% of 2-isobutyl-2,4-dimethyl-1,3-dioxane.

Composition:	Parts
Silica, 90 mesh	70
Chlorinated trisodium phosphate	10
Sodium alkylbenzene sulfonate	3.33
Sodium tripolyphosphate	16.67

After storage, as per Example 4, the perfume odor was unaffected.

EXAMPLE 8

Two perfumery blends were provided. Blend A contained 20% of 2-isobutyl-4-methyl-1,3-dioxane as the principal source of "geranium" odor. Blend B had conventional perfumery materials as the source of geranium character. The blends had the following composition.

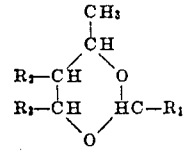
Composition	Parts A	Parts B
Citronellol	200	200
2-isobutyl-4-methyl-1,3-dioxane	200	----------
Cinnamic alcohol	500	500
Thyme oil	30	30
Amyl cinnamic aldehyde	40	40
Linalool		100
Geranyl acetate		100
	970	971

The dishwasher product in Example 6 was modified independently with 0.05% of each blend. After storage as described in Example 4, the odor of Blend A remained unchanged. Conversely, the product with Blend B had less geranium odor after storage.

Having set forth the general nature and specific embodiments of the present invention, the true scope is now particularly pointed out in the appended claim.

What is claimed is:

1. A perfume having the structure:



wherein R_1 is an alkyl group having 4 to 9 carbon atoms; R_2 is selected from the group consisting of hydrogen and a C_1 to C_4 alkyl group; and R_3 is selected from the group consisting of hydrogen and methyl.

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