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CYCLIC KETALS AND ACETALS OF NORBORNANE CARBOXYALDEHYDE

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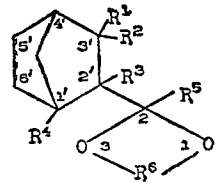
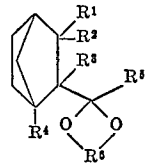
ABSTRACT OF THE DISCLOSURE

Chemical compounds characterized by the structural formula



wherein R^1, R^2, R^3 and R^4 each represent hydrogen or methyl, R^5 represents hydrogen or lower alkyl and R^6 represents a polymethylene radical of from 2 to 4 carbon atoms which is unsubstituted or substituted with lower alkyl groups have very pleasant, strong and long lasting aromas and are useful as components in fragrance compositions. These compounds can be prepared by an acetalization reaction of an appropriate norbornane or norbornene carboxaldehyde or an appropriate norbornyl or norbornenyl alkyl ketone with a dihydric alcohol.

The novel chemical compounds characterized by the structural formula



wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined above are particularly preferred due to their outstanding usefulness as aroma chemicals.

This invention relates to the art of fragrance compositions. More specifically, this invention is directed to a class of compounds that possess characteristics aromas and are useful as components in fragrance compositions and to a class of novel compounds possessing particularly outstanding characteristic aromas.

The art of perfumery began, perhaps, in the ancient cave dwellings of prehistoric man. From its inception, and until comparatively recently, the perfumer has utilized natural perfume chemicals of animal and vegetable origin. Thus, natural perfume chemicals such as the essential oils, for example, oil of rose and oil of cloves, and animal secretions such as musk, have been manipulated by the perfumer to achieve a variety of fragrances. In more recent years, however, research perfume chemists have developed a large number of synthetic odoriferous chemicals possessing aroma characteristics particularly desired in the art. These synthetic aroma chemicals have added a new dimension to the ancient art of the perfumer, since the compounds prepared are usually of a stable chemical nature, are inexpensive as compared with the natural perfume chemicals and lend themselves more easily to manipulation than natural perfume chemicals since such natural perfume chemicals are usually a complex mixture of substances which defy chemical analysis. In contrast thereto, the synthetic aroma chemicals possess

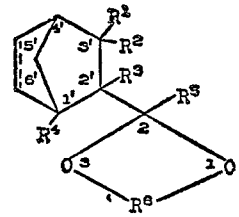
a known chemical structure and may therefore be manipulated by the perfumer to suit specific needs. Accordingly, there is a great need in the art of fragrance compositions for compounds possessing characteristic aromas.

The principal object of the present invention is to provide a new class aroma chemical compounds.

Another object of the present invention is to provide a specific class of aroma chemical compounds having a characteristic aroma which is utilized in the preparation of fragrances and fragrance compositions.

These and other objects, aspects and advantages of this invention will become apparent from a consideration of the accompanying specification and claims.

In accordance with the above objects, there is provided by the present invention a class of compounds characterized by the structural formula

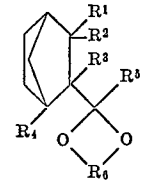


(I)

wherein R^1, R^2, R^3 and R^4 each represent hydrogen or methyl, R^5 represents hydrogen or a lower alkyl and R^6 represents a polymethylene radical of from 2 to 4 carbon atoms which is unsubstituted or substituted with lower alkyls which, as a whole exhibits a characteristic pleasant, strong and long lasting aroma, which is highly useful in the preparation of fragrance compositions and perfumed products.

By the term "lower alkyl" is meant an alkyl group having from 1 to 5 carbon atoms, whether branched or straight chain, such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl and the like. Preferred lower alkyl groups are n-alkyl groups having 1 to 3 carbon atoms inclusive.

Preferred and novel compounds within the scope of Formula I are characterized by the structural formula



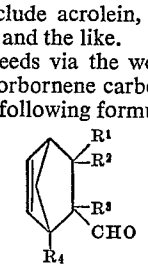
wherein R^1, R^2, R^3, R^4, R^5 and R^6 have the same meaning as defined hereinbefore.

The compounds of the present invention, wherein R^5 is hydrogen, are readily prepared as hereinafter described. In the first step, an appropriate cyclopentadiene is reacted with an α,β-unsaturated aldehyde of the formula

$$R^1R^2C{=}CR^3CHO$$

wherein R^1, R^2 and R^3 are as defined hereinbefore. Illustrative aldehydes include acrolein, methacrolein, crotonaldehyde, 2-pentenal and the like.

The reaction proceeds via the well known Diels-Alder addition to yield a norbornene carboxaldehyde compound characterized by the following formula:



wherein R^1, R^2, R^3 and R^4 are as previously defined. The reaction conditions of the Diels-Alder reaction are not

critical, although elevated temperatures such as 50–150° C. are normally employed.

In the second step, the products of this invention are obtained from the above carboxaldehyde compounds by acid-catalyzed acetalization with a dihydric alcohol such as 1,2-diol, 1,3-diol or 1,4-diol.

The term "1,2-diol" refers to a saturated hydrocarbon compound that has two hydroxy groups attached thereto on adjacent carbon atoms. The term "1,3-diol" refers to a saturated hydrocarbon compound that has two hydroxy groups attached thereto but that are attached to carbon atoms that are separated by one carbon atom. The term "1,4-diol" refers to a saturated hydrocarbon compound that has two hydroxy groups attached thereto but that are attached to carbon atoms that are separated by two carbon atoms.

Representative 1,2-diols which can be utilized in the acetalization reaction include ethylene glycol, 1,2-propanediol, 2,3-butanediol, 3,4-hexanediol, 3,4-heptanediol, 4,5-octanediol, 5,6-decanediol, 6,7-dodecanediol, 2,3-dimethyl-2, 3-butanediol, 2,3-diethyl-2, 3-butanediol, 3,4-diethyl-3, 4-hexanediol and the like.

Representative 1,3-diols which can be utilized in the acetalization reaction include 1,3-propanediol, 1,3-butanediol, 3-methyl-1,3-butanediol, 1,3-pentanediol, 2,4-pentanediol, 3,5-heptanediol, 3,5-dimethyl-3,5-heptanediol, 4,6-diethyl-2,2-dimethyl-4,6-octanediol, 3-ethyl-5-methyl-3,5-nonanediol and the like.

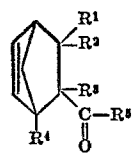
Representative 1,4-diols which can be utilized in the acetalization reaction include 1,4-butane diol, 1,4-pentane diol, and 2,5-hexane diol and the like.

Acid catalysts include organic carboxylic or sulfonic acids as well as mineral acids. Organic sulfonic acids, such as benzenesulfonic acid, p-toluenesulfonic acid and the like are preferred.

The reaction conditions for the acetalization reaction are not narrowly critical, although elevated temperatures, for example 50 to 150° C. are ordinarily necessary to achieve an acceptable rate. It is also desirable to remove the water formed by the reaction as it is formed to drive the reaction to completion. This is easily effected by conducting the reaction under reflux in a solvent, such as benzene or toluene, which forms a minimum boiling azeotrope with water, and separating the water from the distillate.

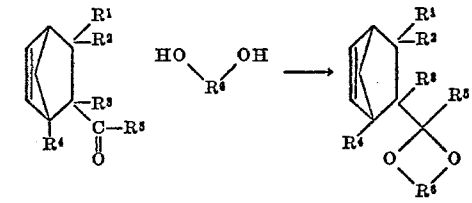
The carboxaldehyde and the dihydric alcohol which are reacted in accordance with this invention are preferably reacted in a mole ratio from about 1.1 to 1 to about 1 to 1.1, however the molar ratio may be from about 2:1 to about 1:2 and still be satisfactory. The catalyst is included in an amount of from about 0.01 to about 1.0 percent, based on the weight of the reactants. Preferably, the amount of catalyst included in the reaction is from about 100 mg. to about 500 mg. per mole of carboxaldehyde. Obviously the amount of catalyst added depends on the particular reactants and the specific reaction conditions employed.

The compounds of this invention, wherein R^5 is lower alkyl, are prepared by reacting a norbornenyl or norbornyl alkyl ketone characterized by the structural formula



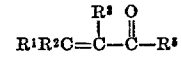
wherein R^1, R^2, R^3, R^4 and R^5 have the same meaning as defined hereinbefore with a dihydric alcohol in a manner as hereinbefore described for the carboxaldehyde

compounds. Such a reaction is illustrated by the following equation:



wherein R^1, R^2, R^3, R^4 R^5 and R^6 have the same meaning as defined hereinbefore.

The norbornenyl alkyl ketones can be prepared in a manner similar to that utilized in preparing the norbornene carboxaldehydes as described hereinbefore. In particular, an appropriate cyclopentadiene is reacted with an α,β-unsaturated ketone of the formula:



wherein R,[1] R^2, R^3 and R^5 are as defined hereinbefore. The reaction proceeds via the well known Diels-Alder addition to yield the desired norbornenyl alkyl ketones.

The norbornyl alkyl ketones can be prepared by suitable hydrogenation of these norbornenyl alkyl ketones.

The novel norbornyl compounds of this invention represented by Formula II can be prepared by the hydrogenation of the corresponding norbornene compound. Alternatively the norbornyl compounds can be prepared by acetalization of the norbornane carboxaldehyde obtained by hydrogenation of the norbornene carboxaldehyde or by acetalization of the norbornyl alkyl ketones in a manner as described hereinbefore.

The compounds of this invention are useful in the preparation and formulation of fragrance compositions such as perfumes and perfumed products due to their pleasing, strong and long lasting aroma. Perfume compositions and the use thereof in cosmetic, detergent and bar soap formulations and the like are exemplary of the utility thereof.

The novel compounds of Formula II are particularly preferred because of the highly desirable aroma characteristics found and the more stable chemical molecule enables a wider scope of use without fear of adverse side reactions.

The compounds of this invention are used in concentrations of from trace amounts up to about 50 percent of the perfume composition into which they are incorporated. As will be expected, the concentration will vary depending on the particular fragrance composition and even within the same composition when compounded by different perfumers. The primary consideration being that the compound is incorporated in an odoriferous amount as desired in a particular fragrance composition.

The following examples will serve to illustrate certain specific embodiments within the scope of this invention and are not to be construed as limiting the scope thereof. The following standard procedure was used for the preparations of the compounds as shown in the following examples:

To a solution of 1 mole of the appropriate norbornene-(or norbornane) carboxaldehyde or alkyl ketone, in 200 ml. of benzene, containing between 200 to 500 mg. of p-toluene sulfonic acid is added 1.1 mole of the dihydric alcohol and the resulting mixture is heated to reflux with stirring until no further water is collected in a Dean-Stark trap. The resulting reaction mixture is poured into cold, dilute sodium carbonate solution, washed with water and concentrated sodium chloride solution, dried over sodium sulfate, filtered, followed by evaporation of the filtrate to give the remainder as the crude product. The crude product is purified by distillation, under reduced pressure, through a short Vigreux type column.

EXAMPLE 1

2-(5'-norbornene-2'-yl)-1,3-dioxolane

Norborn-5-en-2-carboxaldehyde is reacted with ethylene glycol and yields 68.1% of the title compound. This material has a boiling point of 89–91° C. at 10 mm. of Hg having an $n_D^{25}=1,4897$. The product is a colorless liquid. This material was submitted to a fragrance panel for aroma characterization and it was described as having green, cuminic, walnut and raw potato aromas.

EXAMPLE 2

2-(5'-norbornene-2'-yl)-1,3-dioxane

Norborn-5-en-2-carboxaldehyde is reacted with 1,3-propanediol to give the title compound in a yield of 28%. The boiling point of the compound was 126° C. at 30 mm. of Hg and having a $n_D^{25}=1.4905$. This material was submitted to a fragrance panel for aroma characterization and it was described as having camphoraceous, minty, styrene, cucumber and castoreum aromas.

EXAMPLE 3

2-(norborn-2'yl)-1,3-dioxolane

The double bond of norborn-5-en-2-carboxaldehyde is hydrogenated to the corresponding norbornyl compound which is then reacted with ethylene glycol to give the title compound in 44.5% yield. This material has a boiling point of 93° C. at 8.5 mm. of Hg having a $n_D^{25}=1.4835$. This material was submitted to a fragrance panel for aroma characterization and it was described as having earthy, camphoraceous, cibet, green, walnut, bark, raw potato and neroli aromas.

EXAMPLE 4

2-(norborn-2'-yl)-1,3-dioxane

Norbornane carboxaldehyde is reacted with 1,3-propanediol to give the title compound in 77.5% yield. This material had a boiling point of 68–70° C. at 0.85 mm. of Hg having a $n_D^{25}=1.4842$. This material was submitted to a fragrance panel for aroma characterization and it was described as having earthy, woody, raw potato, anise, sweet, vegetable and menthone aromas.

EXAMPLE 5

2-methyl-2-(norborn-5'-en-2'-yl)-1,3-dioxolane

Norborn-5-en-2-yl methyl ketone is reacted with ethylene glycol to give the title compound in a yield of 39.6%. The boiling point of this material is 86° C. at 6 mm. of Hg having a $n_D^{25}=1.4840$. This material was submitted to a fragrance panel for aroma characterization and it was described as having pungent, animal, woody, minty and eucalyptol aromas.

EXAMPLE 6

2-(norborn-5'-en-2'-yl)-5,5-dimethyl-1,3-dioxane

Norborn-5-en-2-yl carboxaldehyde was reacted with 2,2-dimethyl-1,3-propanediol to obtain the title compound in a yield of 62.5%. This material had a melting point of 65° C. and a boiling point at 86° C. at 1.2 mm. of Hg. It is found to be soluble in benzene. This material was submitted to a fragrance panel for aroma characterization and it was described as having a cucumber, green, castoreum, rancid and milk-barn aromas.

EXAMPLE 7

2-methyl-2-(norborn-2'-yl)-1,3-dioxolane

The double bond of norborn-5-en-2-yl methyl ketone is hydrogenated to obtain the corresponding norbornyl methyl ketone over palladium on charcoal. Norbornyl methyl ketone is reacted with ethylene glycol to obtain the title compound in a yield of 69.6%. The resulting product has a boiling point of 65° C. at 3.5 mm. of Hg having an $n_D^{25}=1.4775$. This material was submitted to a fragrance panel for aroma characterization and it was described as having eucalyptus, woody, pine, menthone, green and fecal aromas.

EXAMPLE 8

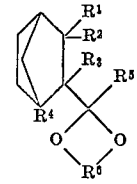
2-(norborn-2'-yl)-5,5-dimethyl-1,3-dioxane

Norbornyl carboxaldehyde is reacted with 2,2-dimethyl-1,3-propanediol to obtain the title compound in an 82.4% yield. This material has a melting point at 73° C. and was a solid, white material at room temperature. This material was submitted to a fragrance panel for aroma characterization and it was described as having, fruity, apple, winey, rasberry, acetic and butter aromas.

While the invention has been described herein with regard to certain specific embodiments, it is not so limited. It is to be understood that variations and modifications thereof may be made by those skilled in the art without departing from the spirit and scope of the invention.

The embodiments of this invention in which a particular property or privilege is claimed are defined as follows:

1. A compound characterized by the structural formula



wherein R^1, R^2, R^3 and R^4 each represent hydrogen or methyl, R^5 represents hydrogen or a lower alkyl and R^6 represents a polymethylene radical of from 2 to 4 carbon atoms which is unsubstituted or substituted with no more than four lower alkyls of from 1 to 3 carbon atoms.

2. A compound as defined in claim **1** which is 2-(norborn-2'-yl)-1,3-dioxolane.

3. A compound as defined in claim **1** which is 2-(norborn-2'-yl)-1,3-dioxane.

4. A compound as defined in claim **1** which is 2-methyl-2-(norborn-2'-yl)-1,3-dioxolane.

5. A compound as defined in claim **1** which is 2-(norborn-2'-yl)-5,5-dimethyl-1,3-dioxane.

References Cited

UNITED STATES PATENTS

3,455,955	7/1969	Chang	260—340.9
3,542,810	11/1970	Roudabush et al.	260—340.9
3,625,977	12/1971	Hamb	260—340.7
3,679,756	7/1972	Kretschmar et al.	260—340.9

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