

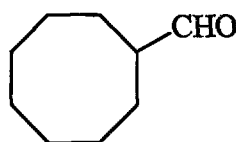
Utilization of Bicyclic Aldehydes as Odoriferous Agents

Field of the Invention

This invention relates to the use of special bicyclic aldehydes obtainable by partial or complete hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes as perfumes. By "bicyclo[3.3.0]oct(adi)enes" are meant both bicyclo[3.3.0]octadienes and bicyclo[3.3.0]octenes. By "(di)methyl-substituted" is meant that the bicyclic system may bear either one or two methyl groups as substituents.

Prior Art

The hydroformylation of cyclic dienes is known from the literature. For example, A. Spencer describes the hydroformylation of inter alia 1,3- and 1,5-cyclooctadiene in the presence of special rhodium catalysts in **Journal of Organometallic Chemistry 1997, 124, pages 85 to 91**. **JP 58/21638** describes a process for the production of dialdehydes in which unconjugated diolefins are reacted with hydrogen and carbon monoxide in a water-immiscible solvent in the presence of a rhodium catalyst. Cyclooctane aldehyde (1)



(1)

is disclosed in **US 3,985,769** as a raw material for the production of acetal derivatives with perfume properties, its olfactory properties being described as "intensively green".

Judging by demand, many natural perfumes are available in totally inadequate quantities. Accordingly, it is clear that there is a constant

demand in the perfume industry for new perfumes with interesting perfume notes in order to extend the range of naturally available perfumes and to be able to make the necessary adaptations to changing fashion trends and to satisfy the continuously increasing demand for odor enhancers for products
5 of everyday use, such as cosmetics and cleaning products.

In addition, there is generally a constant need for synthetic perfumes which can be favorably produced in a consistent quality and which have desirable olfactory properties, i.e. pleasant, near-natural and qualitatively new odor profiles of adequate intensity, and which are capable of
10 advantageously influencing the fragrance of cosmetic and consumer products. In other words, there is a constant need for compounds which have characteristic new odor profiles coupled with high staying power, intensity of odor and emanative power.

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Description of the Invention

It has surprisingly been found that special bicyclic aldehydes obtainable by partial or complete hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes have remarkable olfactory properties. Over and above their special odor characteristic, which is characterized by
20 a broad range with complex nuances, the compounds are distinguished by high staying and emanative power. In addition, they are eminently suitable as perfume boosters. A perfume booster is understood to be a substance which is capable of lastingly intensifying the olfactory impressions of the components of a multicomponent system, i.e. a mixture of two or more
25 perfumes.

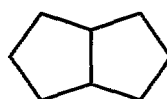
The present invention relates to the use of bicyclic aldehydes obtainable by partial or complete hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes as perfumes.

The present invention also relates to the use of bicyclic aldehydes
30 obtainable by partial or complete hydroformylation of optionally (di)methyl-

substituted bicyclo[3.3.0]oct(adi)enes as perfume boosters. 3-formyl bicyclo[3.3.0]octane is particularly preferred for this use.

The aldehydes to be used in accordance with the invention are advantageously prepared by hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes which have a bicyclic system as a common backbone. The backbone is illustrated by formula (2) below, but without the (optional) methyl groups or C=C double bonds:

10



(2)

The system (2) contains one or two C=C double bonds. If two C=C double bonds are present, they are not immediately adjacent. One or two methyl groups may optionally be present.

The hydroformylation is a reaction known to the expert which was discovered by Roelen in 1938. In this reaction, alkenes are converted into aldehydes with carbon monoxide and hydrogen. The reaction is also known as oxosynthesis.

If optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes are used as starting materials for the purposes of the present invention, the hydroformylation may be carried out in part or completely. In the case of partial hydroformylation, one olefinic double bond remains intact per molecule of the starting compound while only the other is hydroformylated; in the case of complete hydroformylation, two CHO groups are introduced into the molecule. If, however, compounds containing only one C=C double bond per molecule are used as starting materials, only complete hydroformylation is of course possible.

The odor profile of the hydroformylation products according to the invention is original and novel. In perfume compositions, they enhance

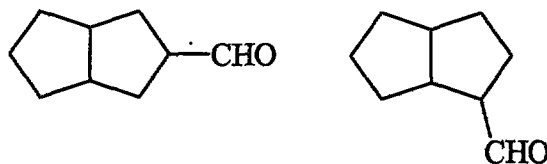
harmony and emanation and also staying power, the particular dosage being adapted to the perfume note required taking the other constituents of the composition into account.

5 The fact that the hydroformylation products according to the invention have interesting perfume notes was not foreseeable and is confirmation of the general experience that the olfactory properties of known perfumes are not necessarily an indication of the properties of structurally related compounds - in the present case cyclooctane aldehyde (1) for example - or mixtures thereof because neither the mechanism of
10 odor perception nor the influence of chemical structure on odor perception has been sufficiently researched, i.e. it cannot normally be predicted whether a modified structure or special mixing ratios of known perfumes lead at all to changes in the olfactory properties and whether these changes may be regarded as positive or negative.

15 By virtue of their odor profiles, the hydroformylation products according to the invention are also particularly suitable for modifying and enhancing known compositions. Particular emphasis is placed above all on their outstanding intensity of odor which contributes quite generally towards the refinement of compositions.

20 Also remarkable is the way in which the hydroformylation products according to the invention round off and harmonize the perfume notes of a broad range of known compositions without unpleasantly dominating them in any way.

(3)2-formyl bicyclo[3.3.0]octane (3) is most particularly suitable for
25 use as a perfume and/or perfume booster in accordance with the invention. Accordingly, it is of particular advantage to use (3)2-formyl bicyclo[3.3.0]octane in air fresheners for example. In addition, it has been found that compound (3) may be used with particular advantage for enhancing citrus notes in cleaning compositions.



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(3)

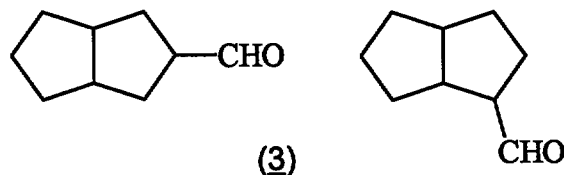
The quantities in which the hydroformylation products according to the invention are used in perfume compositions are between 0.001 and 70% by weight, based on the mixture as a whole. The hydroformylation products according to the invention and corresponding compositions may be used both for perfuming cosmetic preparations, such as lotions, creams, shampoos, soaps, salves, powders, aerosols, toothpastes, mouthwashes, deodorants, and in extract perfumery. They may also be used for perfuming technical products and detergents and cleaning compositions, fabric softeners, textile treatment compositions and tobacco. For perfuming these various products, the compositions are added to them in an olfactorily effective quantity, more particularly in a concentration of 0.05 to 2% by weight, based on the product as a whole. However, these values are not intended to represent limits because the experienced perfumist can still obtain effects with lower concentrations or can build up new complexes with even higher concentrations.

The following Examples are intended to illustrate the invention without limiting it in any way.

25

Examples

1. Preparation of 3(2)-formylbicyclo[3.3.0]octane (3)



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2 Moles (216 g) of cis-bicyclo[3.3.0]oct-2-ene (manufacturer: Wiley; gas chromatographic purity: 99%) were introduced into an autoclave together with 1.7 mmols (1.175 g) of a rhodium catalyst with the formula $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ and 19 mmols (5 g) of triphenyl phosphine and reacted
10 with a 1:1 mixture of hydrogen and carbon monoxide with intensive stirring for 5 hours at 100°C under a pressure of 60 kg/cm² and in the absence of solvent. For working up, the contents of the reactor were filtered and distilled through a 20 cm Vigreux column.

Fractionation into educt and (3)2-formyl bicyclo[3.3.0]octane (3) was
15 carried out in a spinning band column. 132 g of (3)2-formyl bicyclo[3.3.0]octane were obtained (boiling point: 97°C/20 mbar).

Odor description: green, herby

**CLAIMS**

1. The use of bicyclic aldehydes obtainable by partial or complete hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes as perfumes.
- 5 2. The use of (3)2-formyl bicyclo[3.3.0]-octane as a perfume.
3. The use of bicyclic aldehydes obtainable by partial or complete hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes as a fragrance booster.
4. The use of (3)2-formyl bicyclo[3.3.0]-octane as a fragrance booster.
- 10 5. The use of bicyclic aldehydes obtainable by partial or complete hydroformylation of optionally (di)methyl-substituted bicyclo[3.3.0]oct(adi)enes in cosmetic preparations, technical products or in alcohol-based perfumery.
6. The use of (3)2-formyl bicyclo[3.3.0]-octane in cosmetic
15 preparations, technical products or alcohol-based perfumery.