

1

3,709,929

4-METHYL-2-PENTANOL CROTONATE

Fritz Exner and Theodor Leidig, Holzminden, Germany,
assignors to Haarmann & Reimer Gesellschaft mit
beschränkter Haftung, Holzminden, Germany

No Drawing. Filed Sept. 21, 1970, Ser. No. 74,228
Claims priority, application Germany, Apr. 10, 1970,
P 20 17 208.1

Int. Cl. C07c 69/56

U.S. Cl. 260—486 R

1 Claim

ABSTRACT OF THE DISCLOSURE

Subject of the invention is 4-methyl-2-pentanol crotonate, a process for its production whereby 4-methyl-2-pentanol is esterified with crotonic acid and the use of the crotonate for perfume compositions and as an odorant.

This invention relates to the crotonic acid ester of 4-methyl-2-pentanol, to its preparation and to its application.

The compound according to this invention can be obtained by esterification methods known per se, preferably by the direct esterification of crotonic acid with 4-methyl-2-pentanol, the water of reaction formed preferably being removed azeotropically, in the presence of an acid catalyst, for example concentrated sulphuric acid or p-toluene sulphonic acid, and a hydrocarbon boiling at 80 to 150° C., preferably toluene or xylene, as entraining agents.

The ester according to the invention is distinguished by desirable odoriferous properties and adds a valuable odorant to the perfume materials hitherto available for synthesizing fruit-like notes.

For some years now, the fruit-like note, partly dominating, partly as a nuance of an odor complex, has been acquiring increasing significance in the manufacture of perfumes for general use and in the synthesis of certain types of odor in fine perfumery. This may be attributable to the fact that an awareness of culinary odors is associated more or less unconsciously with a feeling of well-being.

The odorants preferably used for the synthesis of fruit-like notes, such as iso-amyl acetate, hexyl acetate, ethyl acetate and other esters of lower fatty acids, readily bring to mind undesirable notions of bonbons or solvents or commercial products. For this reason they are not easy to handle in the composition of perfumes and have to be harmonically rounded off in terms of odor by skillfully combining several of these substances in order to restrict the occurrence of aesthetically unpleasant notes.

4-methyl-2-pentanol crotonate does not have any of these disadvantages. It has a very pleasant, pure fruit-like note reminiscent in particular of plum and apple preserves. It differs from conventional fruit-like odorants not only in its type of odor but also in the fact that it can be used more easily and more widely. Although distinct effects in the perfume composition can be obtained even with small quantities of the odorant, it can also be used in a high concentration in the composition or even without any other odorants for perfuming preparations by virtue of its aesthetically pleasing odor, without the aforementioned negative side effects encountered in conventional fruity odorants.

By virtue of its type of odor and its service properties, the compound according to the invention can be used for a very wide variety of applications. It is suitable for use in perfume compositions for numerous end products of the cosmetics, fine-perfumery, detergent and chemical specialties industries.

In high concentrations it is preferably used for plum

2

notes, in average concentrations as the main carrier of the fruit-like character in conjunction with other suitable odorants for the production of other fruit-like notes such as apple, pear, peach and grape. In low concentrations, 4-methyl-2-pentanol crotonate is advantageously also used in compositions where the dominating odor note cannot be regarded as fruit. In this way, a "natural" character can be imparted to some of these compositions.

The possibilities of composition are further enriched by using 4-methyl-2-pentanol crotonate insofar as novel extremely harmonic odor accords can be obtained with this odorant, especially by combining it with flower and green odorants.

EXAMPLE 1

The following formulation is given as an example of the preparation of a perfume with a plum-like odor which is a suitable fragrance for dishwashing detergents:

β,γ-hexanol isobutyrate, 10%	5
Bergamot oil, Reggio	10
Geraniol	100
Geranyl acetate	170
Citronellyl acetate	40
Citronellyl isobutyrate	50
Citronellol	50
Phenylmethyl glycidic acid ethyl ester, 1%	5
Terpineol	20
Phenylethyl isobutyrate	50
4-methyl-2-pentanol crotonate	500
.....	1000

4-methyl-2-pentanol crotonate produces a pleasant full-fruit plum note without being found to be overdosed in this concentration as is often the case with conventional plum odorants.

A dishwashing detergent scented with this formulation can have the following composition for example:

Sodium alkyl sulphonate or sodium alkyl benzosulphonate	200
Fatty alcohol ether sulphate	70
Coconut fatty acid diethanolamide	30
Sodium chloride	20
Water, coloring and skin preservative	677
Perfume oil	3
.....	1000

EXAMPLE 2

The following formulation is given as an example of the preparation of a flower bouquet with a freshening fruit nuance which is suitable for perfuming creams:

Cumyl propionaldehyde	15
Linalool	50
Linalyl acetate	30
Terpinyl acetate	25
Terpineol	60
Geraniol	150
Phenylethyl alcohol	100
Phenylethyl dimethyl carbinol	100
Hydrocinnamic alcohol	30
Farnesol	100
Hydroxycitronellal	170
α-Amylcinnamic aldehyde	100
α-Ionone	20
Coumarin	20
Ethylene brassylate	10
4-methyl-2-pentanol crotonate	20
.....	1000

The somewhat flat, harmless, phantasy bouquet is distinctly freshened and aesthetically improved by the small

3

addition of 4-methyl-2-pentanol crotonate. The fruit nuance introduced gives the perfume more freshness and a natural character.

A skin cream perfumed with this composition can be prepared as follows for example:

Phase A: 50 g. of oleic acid decyl ester, 125 g. of glycerine monostearate (self-emulsifying), 50 g. of paraffinum per liquidum, 20 g. of cetaceum DAB 7, 1 g. of p-hydroxybenzoic acid propyl ester.

Phase B: 720 g. of distilled water, 1 g. of p-hydroxybenzoic acid methyl ester, 30 g. of sorbitol, 3 g. of perfume oil.

Phase A and phase B are heated to 75° C., after which phase B is stirred into phase A, cooled with stirring to 40° C. and perfumed.

EXAMPLE 3

The following formulation is given as an example of the preparation of a perfume with a lemon odor which is suitable for perfuming an insect spray:

n-Octanol, 10%	10
n-Nonanol, 10%	20
n-Decanal, 10%	20
Terpinyl acetate	60
Linalyl acetate	50
Geranyl acetate	10
Geraniol	100
Linalool	30
Terpineol	30
Nerolidol	30
Petit grain oil, Parag.	30
Limonene	450
Citral	60
4-methyl-2-pentanol crotonate	100
	1000

In the lemon odor of the perfume, the fruit component is enhanced by the 4-methyl-2-pentanol crotonate, the odor is fuller and more pleasant.

An insect spray perfumed with this composition can be prepared as follows, for example:

2,2-dichlorovinyl dimethyl phosphate	5
Epichlorohydrin	2
Isopropyl alcohol	40
Odorless kerosene	100
Perfume oil	3
Monofluorotrichloromethane 11	425
Difluorodichloromethane 12	425
	1000

2,2-dichlorovinyl dimethyl phosphate and epichlorohydrin are dissolved in isopropyl alcohol, odorless kerosene and perfume oil are added, the can is closed with a valve and, after pressure-filling, is filled with the propellant gas mixture 11/12 50:50.

EXAMPLE 4

The following formulation is given as an example of the preparation of a lavender composition which is suitable for perfuming tissues:

4

Rosemary oil, tunes.	50
Lavandin oil, 30/32	300
Petit grain oil, Parag.	50
Linalyl acetate	100
Linalool	100
Terpinyl acetate	100
Terpineol	50
Amyl salicylate	40
Nerolidol	100
Octenol acetate	5
Benzyl salicylate	15
Patchouli oil	20
Coumarin	10
Ethylene brassylate	10
4-methyl-2-pentanol crotonate	50
	1000

The herb-like, lavandin oil note is sweetened by the 4-methyl-2-pentanol crotonate and displaced more towards the lavender type.

Tissues perfumed with this composition can be produced by impregnating paper webbing with a solution which can have the following composition for example:

	Percent
Alcohol	80
Perfume oil	3
Distilled water	17
	100

EXAMPLE 5

A mixture of 6 mols=516 g. of crotonic acid, 5 mols=560 g. of 4-methyl-2-pentanol, 20 g. of p-toluene sulfonic acid and 2 liters of xylene is heated under reflux in an apparatus provided with a water separator until no more water is separated (theoretical 90 g.).

In general this is achieved after 4 hours when 85 cc. of the water have been separated off.

The reaction mixture is washed first with 2 litres of 10% soda solution to remove the acids and then with water until the reaction mixture reacts neutrally.

After the xylene has been distilled off, the product is distilled in vacuo, giving at B.P.₁₄: 80-85° C. 780 g. or 91.7% of the theoretical of crude crotonic acid 4-methyl-2-pentanol ester.

The crude ester is re-washed with soda solution and water and then re-distilled. Yield 764 g.=89.5% of the theoretical.

B.P.₁₆: 86-88° C.; D₄²⁰: 0.875; n_D²⁰: 1.4324.

We claim:

1. 4-methyl-2-pentanol crotonate.

References Cited

Kulka, K., Chemical Abstracts, vol. 58, 7781h, 1963.

LORRAINE A. WEINBERGER, Primary Examiner

P. J. KILLOS, Assistant Examiner

U.S. Cl. X.R.

252-522