

1

2,710,825

PERFUME COMPOSITION

Wilbur Arthur Lazier, North Adams, Mass., and Carl Bordenca, Birmingham, Ala., assignors to Food Machinery and Chemical Corporation, San Jose, Calif., a corporation of Delaware

No Drawing. Application April 16, 1954, Serial No. 423,837

3 Claims. (Cl. 167-94)

This application is in part a continuation of copending application Serial No. 222,292, filed April 21, 1951, now abandoned, which was in turn a continuation-in-part of U. S. Patent 2,584,539 issued February 5, 1952.

The present invention relates to perfumes, particularly to high quality perfumes that are blended from relatively easily available ingredients.

The blending of perfumes is perhaps the oldest of arts and has been widely practiced in attempts to synthesize natural perfumes. New blending ingredients are continually sought, however, to widen the range of individual odors that are available for blending. Each new ingredient enables many new combinations of scents so that natural perfumes can be more closely duplicated or completely new mixtures made to please the sense of smell.

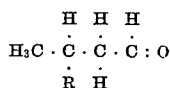
The most desirable perfume ingredients are those that have a low volatility and therefore long persistence. Perfume blends normally contain some highly persistent ingredients, and if relatively volatile scent-contributing materials are also present, the scent will undergo a major change upon exposure by reason of the selective evaporation.

Among the objects of the present invention is the provision of new perfume oils and blends.

Further objects of the present invention include the provision of novel perfumes with fragrance-imparting ingredients of relatively low volatility.

Additional objects of the present invention are novel perfumes made with ingredients and intermediates that are easily available.

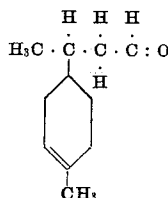
It has been discovered that the class of compounds having the formula:



where R is an alkyl-substituted, six-carbon nonbenzenoid alicyclic hydrocarbon group, are highly effective perfume ingredients. These compounds in pure condition have a citronella-like odor and contribute to a perfume a floral and citrus background with a characteristic lift. The odors are highly persistent and quite powerful so that only a very small proportion is needed for blending.

The various individual members of the above described class of compounds all have slight differences in odor, but these odors closely resemble each other and in general can be used interchangeably for blending purposes.

One preferred example of the new perfume ingredients is beta-(4-methyl-Δ3-cyclohexenyl) butyraldehyde, which structurally is:

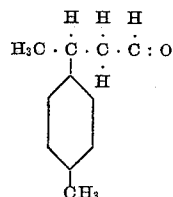


2

This compound is readily made by reacting limonene (dextrorotatory or laevorotatory) or its optically inactive isomer dipentene, with carbon monoxide and hydrogen, as more fully explained in the above-identified parent U. S. patent, the disclosure of which is hereby included in this specification as though fully set forth herein. In its optically active form it boils at 72° to 74° C. under a pressure of one millimeter of mercury, at 27° C. shows an index of refraction for the yellow sodium D line of 1.477. Its specific optical rotation for the yellow sodium D line at 27° C. is 15.3 degrees.

Limonene is found in appreciable quantities in citrus peelings, large amounts of which are normally discarded by the fruit canning industry. The other reactants, carbon monoxide and hydrogen are also readily available, and because of these features the perfume ingredients of the invention are easily produced at a relatively low cost. Care must be taken, however, not to attempt the reaction with catalysts that are too highly active in hydrogenation reactions, inasmuch as such catalysts cause the production of tars and foul-smelling products from which the desired pleasant smelling aldehyde cannot be recovered. The reaction conditions specified in the parent case provide very satisfactory yields of aldehyde suitable for blending.

Another specific example of the above-described class of perfume ingredients is beta-(4-methyl-cyclohexyl) butyraldehyde, the structure of which is:



This compound can be readily formed by hydrogenating the beta-(4-methyl-Δ3-cyclohexenyl)-butyraldehyde described above. The hydrogenation is suitably effected in the conventional manner by shaking the unsaturated aldehyde at room temperatures with Raney nickel or finely divided platinum catalyst, and hydrogen at pressures of at least about fifty pounds per square inch. Higher temperatures and different hydrogenation catalysts can also be used. Furthermore, some amounts of the saturated aldehyde usually accompany the unsaturated aldehyde production, as is shown in the parent case, and can be separately recovered. In addition, the reaction of limonene, or dipentene, with carbon monoxide and hydrogen can be effected with an excess of hydrogen, about two or more times the proportions shown in the prior case, thereby increasing the direct production of the saturated aldehyde. The saturated aldehyde boils at 58° to 59° C. under a pressure of one millimeter of mercury and has an index of refraction of 1.465 for the yellow sodium D line at 28° C.

Other members of the above-described class of perfume ingredients can be prepared from other sources. Such other sources may have the alicyclic ring substituted with an alkyl radical other than methyl, and the methyl or other substituted radical may be positioned in different places on the ring. The alicyclic ring may also have two double bonds, if desired, without appreciably altering the odor of the aldehyde.

The present invention also encompasses the use as fragrance-imparting agents of the various optical isomers of the aldehydes set forth above, including dextro, laevo and racemic forms. The aldehydes have at least two asymmetric carbon atoms in the molecule, one at the beta position with respect to the aldehyde, and the other in the ring at the position where it is linked to the

beta-positioned carbon. A variety of different dextro and laevo forms can accordingly be obtained, as is well known.

That the basic principles of perfumery and perfume compounding are complex has long been recognized by all associated with the perfume industry, whether they be manufacturers or experimentors. In the "Schimmel Briefs" No. 15 published June 1936, for example, it is stated that:

"The very nature of perfume compounding is so intricate, not to say intangible, and there are so many considerations entering into it, that definite rules for the procedure can hardly be set down in black and white."

It is difficult to generalize on the procedure for perfume compounding because, as has been pointed out, every new composition is subject to variations and modifications which are normally ascertained de novo by experimentation. However, certain fundamental classes of perfume components are well recognized in the field.

According to Riegel, "Industrial Chemistry," 5th ed., p. 645 (1949), a perfume may be said to consist of three parts: the odoriferous or fragrance-imparting part, the fixative part and the diluent. The odoriferous component, as the name indicates, serves to impart the odor or fragrance to the perfume. Thus in the creation of a perfume compound, consideration must be given to the intensity of its odor, and sufficient of the odoriferous constituents are employed to impart the desired fragrance to the final blend. In this way, while the percentage composition of a perfume may indicate a component to be present in rather minor quantity, its contribution to the fragrance of the finished product may be quite dominant. For example, although p-cresol-methyl ether or methyl acetophenone may be present in very small quantities, contribution to the final perfume odor is quite pronounced.

In this connection it should be pointed out that among the distinctive properties of the aldehydes of the present invention are the intensity and persistence of their odor. In a comparative study with oil of cloves, for instance, beta-(4-methyl- Δ 3-cyclohexenyl) butyraldehyde was found to be detectable and fragrance-imparting in one-fifth the concentration of this conventional oil. When compared to citral too, the odor of the subject aldehyde was found to be much stronger and more lasting. In addition, the butyraldehyde imparts a characteristic "greenness" or freshness to the compounded product.

The fixatives serve primarily to control the degree of volatilization of the different more or less volatile components of the perfume. In some instances these materials may possess their own distinctive odors and contribute as well to the emergent odor. Because of this a given perfume type may require a particular fixative which would not be suitable for a perfume of another type. Generally, however, a maximum efficiency is obtained through the use of mixtures of suitable fixatives. Examples of conventional fixatives are musk xylene, civetone, musk ambrette, coumarin, vanillin and oakmoss.

The function of the perfume diluent is primarily that of reduction and masking of odor of the blend and in a smaller measure to contribute to the odor of the final product. Examples of this constituent are bergamot oil, limonene, benzyl benzoate, and ethanol.

In view of the above it should be apparent that only generalizations can be made in regard to the function of the various perfume components. For example, coumarin, heliotropin and vanillin are generally considered as sweeteners but may serve in some instances as fixatives. Bergamot oil is probably more of an extender or perfume diluent although its contribution to the floral character of the perfume is quite definite. Vetiver and patchouli oils serve in part as fixatives and to a lesser extent to impart or intensify woody notes or wood-like odors.

Without limiting the invention in any way, but merely

to facilitate the practicing of the present invention by others, there are given below some representative perfume formulations in which the new aldehydic fragrance-imparting agents are effectively incorporated.

Oriental perfume oil

	Parts by weight
Coumarin	175
Vanillin	50
Ethyl vanillin.....	5
Musk xylene.....	45
Rose oil.....	20
Bergamot oil.....	240
Oakmoss tincture.....	25
Patchouli oil.....	40
Vetiver oil.....	20
Neroli oil.....	25
Lavender oil.....	5
Jasmine oil.....	65
Ylang-ylang	15
Geraniol	10
Geranium oil.....	10
Benzyl benzoate	240
Beta-(4-methyl- Δ 3-cyclohexenyl) butyraldehyde.....	10
	1,000

Pine oil

	Parts by weight
Bornyl acetate.....	190
Geranium oil.....	95
Cassia oil.....	40
Clove oil.....	50
Petitgrain oil.....	50
Lavender oil.....	240
Bergamot oil.....	195
Terebene	50
Musk ambrette.....	20
Coumarin	30
Patchouli oil.....	10
Beta-(4-methyl-cyclohexyl) butyraldehyde.....	30
	1,000

Santal oil

	Parts by weight
Sandalwood oil.....	290
Cedarwood oil.....	290
Clove oil.....	50
Cassia oil.....	20
Patchouli oil.....	30
Geranium oil.....	140
Cananga oil.....	50
Bergamot oil.....	50
Musk ambrette.....	20
Coumarin	20
Oakmoss absolute.....	10
Beta-(4-methyl- Δ 3-cyclohexenyl) butyraldehyde.....	30
	1,000

Apple blossom oil

	Parts by weight
Terpineol	300
Bois de rose oil.....	200
Cananga oil.....	40
Phenylethyl alcohol.....	200
Benzaldehyde	2
Benzyl alcohol.....	70
Peru balsam.....	30
Gamma undecalactone.....	25
Musk xylene.....	50
Heliotropin	50
Phenylacetaldehyde	20
Beta-(4-methyl- Δ 3-cyclohexenyl) butyraldehyde.....	10
Indole	3
	1,000

A high grade oriental perfume was made from a mixture of 199 parts of the above oriental perfume oil, 798 parts of 96 per cent ethanol, and 3 parts of the standard tincture of civet, all parts being by weight. The other oils can be similarly compounded into high quality perfumes, adding ethanol or other diluents thereto and other fragrance-imparting agents if desired. Thus a pleasing apple blossom perfume was prepared by mixing 500 parts by weight of the above apple blossom oil and 500 parts by weight of 96 per cent ethanol. The pine oil was made into a perfume by mixing 200 parts of it with 800 parts of 96% ethanol. 200 parts of the santal oil were similarly compounded with 800 parts of 95 per cent ethanol.

The proportions of the various ingredients in the above formulations can be varied over a considerable range. The butyraldehydes even in a concentration of 1/2 per cent by weight impart their characteristic lift. They are most suitable in concentrations of up to about 10 per cent by weight. Usually diluents constitute the major proportion of the compounded perfumes, e. g. normally between about 50 and 90 per cent by weight. The proportion of fixatives generally varies from say 1 to 5 per cent by weight of the total composition.

The aldehydes of the present invention make not only good fragrance-imparting agents for perfumes in themselves, but they can be used as intermediates in the preparation of other such agents and hence other desirable perfumes. Thus by oxidizing the aldehyde to the corresponding acid, there is produced a butanoic acid having a very pleasing rum-butter odor. This reaction is conveniently and rapidly carried out in a cold (10° C.) mixture of benzene and dilute sulfuric acid (30 per cent acid by weight) containing potassium dichromate. The butanoic acids can be esterified by conventional techniques to produce other compounds having odors resembling those of spices, the odor of the ethyl ester being of strong nutmeg-like character.

The aldehydes of the present invention can also be reduced to the corresponding alcohols which have a strong and persistent rose odor. These alcohols can also be esterified to provide compounds having a sweet floral (geranium-like) odor. For details of these procedures see the copending patent application of Wearn and Bordenca, Serial No. 718,609 filed December 26, 1946, now Patent No. 2,556,150.

The aldehydes of the invention can also be condensed with ketones or other aldehydes to form condensation

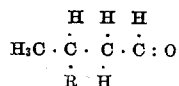
products having a generally peach-like odor. Such processes are disclosed in the copending application of Wearn and Bordenca, Serial No. 721,874 filed January 13, 1947, now Patent No. 2,519,327.

Still further fragrance-imparting ingredients can be made by converting the aldehydes of the invention to the corresponding acetals. Thus by reacting the aldehyde with ethyl orthoformate, a diethyl acetal is formed having a woody, cedar-like odor. This reaction can be readily carried out by contacting equal parts by weight of the aldehyde and ethyl orthoformate in ethanol solution in the presence of solid aluminum chloride catalyst. The reaction can be carried out at room temperature, but can be accelerated by heating to higher temperatures up to the point at which vigorous refluxing takes place.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. A perfume composition containing a fragrance-imparting proportion of a compound having the formula



where R is an alkyl-substituted nonbenzenoid six-carbon cyclic hydrocarbon group, along with a major proportion of other fragrance-imparting agents and perfume diluents.

2. The perfume composition of claim 1 wherein the said fragrance-imparting compound is a beta(4-methyl-Δ3-cyclohexenyl) butyraldehyde.

3. The perfume composition of claim 1 wherein the said fragrance-imparting compound is a beta-(4-methyl-cyclohexyl) butyraldehyde.

References Cited in the file of this patent

UNITED STATES PATENTS

2,327,066	Roelen	Aug. 17, 1943
2,437,600	Gresham et al.	Mar. 9, 1948
2,584,539	Bordenca	Feb. 5, 1952

FOREIGN PATENTS

888,667	France	Sept. 13, 1943
---------	--------	----------------