

[54] **NOVEL PERFUMERY USES OF
 π -CYANOTRICYCYLENE**

[75] **Inventors:** Braja Dulal Mookherjee, Matawan;
Venkatesh Kamath, Red Bank, both
of N.J.; Edward J. Shuster,
Brooklyn, N.Y.

[73] **Assignee:** International Flavors & Fragrances
Inc., New York, N.Y.

[22] **Filed:** Mar. 10, 1975

[21] **Appl. No.:** 556,874

[52] **U.S. Cl.** 252/522; 260/464; 260/468 G;
260/675.5

[51] **Int. Cl.²** A61K 7/46; C11B 9/00

[58] **Field of Search** 252/522; 260/675.5, 464

[56] **References Cited**

UNITED STATES PATENTS

2,730,548 1/1956 Bluestone et al. 260/586 G

OTHER PUBLICATIONS

Arctander, "Perfume and Flavor Chemicals" (1969):
Compound Nos. 641, 764, 1064, 1439 and 1451.

Primary Examiner—Herbert Levine

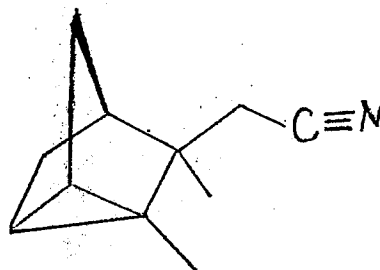
Assistant Examiner—G. E. Schmitkons

Attorney, Agent, or Firm—Arthur L. Liberman, Esq.;
Harold Haidt, Esq.

[57]

ABSTRACT

Processes and compositions are described for altering the aroma of consumable products including perfumes, perfume compositions and perfumed articles utilizing as the essential ingredient an organic tricyclic derivative having the formula:



4 Claims, 2 Drawing Figures

EXAMPLE I
TT - cyanotricycylene

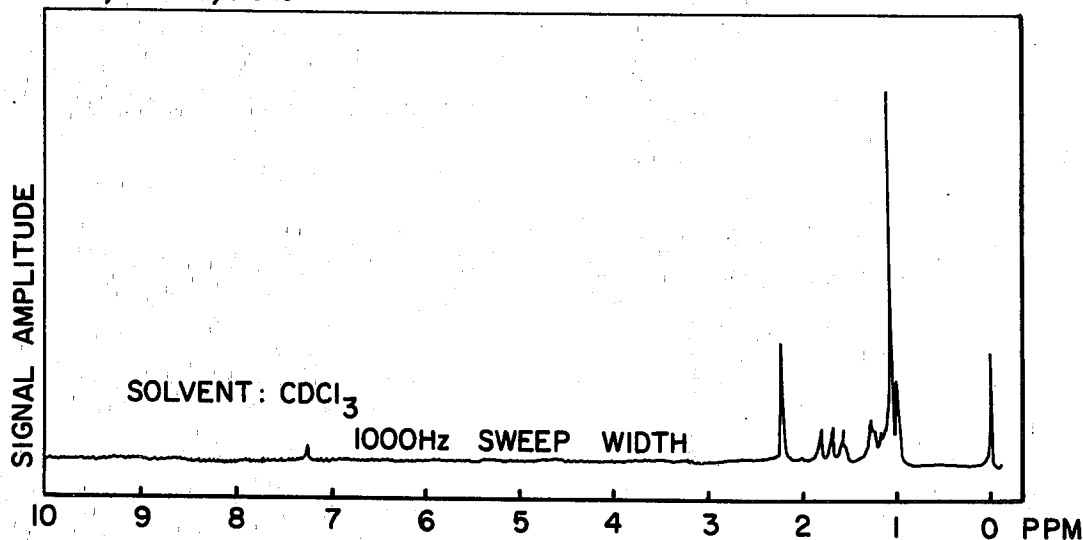
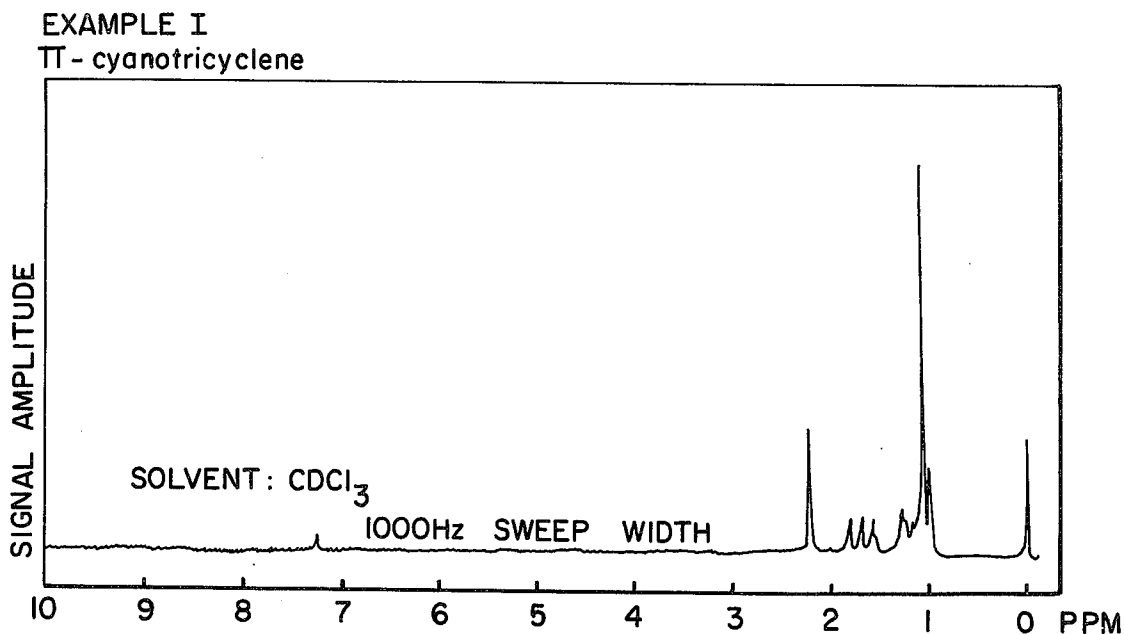
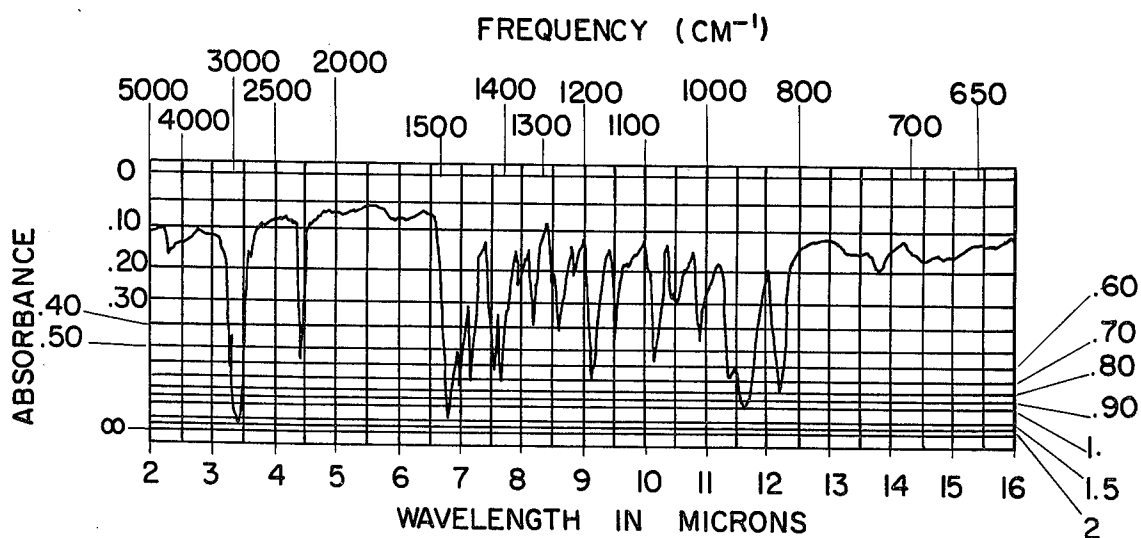


FIG. 1



EXAMPLE I
TT - cyanotricyclene

FIG. 2

NOVEL PERFUMERY USES OF π -CYANOTRICYCYLENE

BACKGROUND OF THE INVENTION

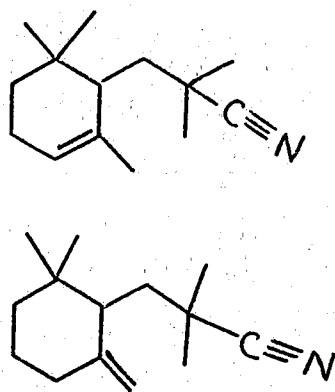
There is a continuing search for materials having desirable fragrance properties. Such materials are sought either to replace costly natural materials or to provide new fragrances or perfume types which have not heretofore been available. Especially desirable qualities for substances having interesting fragrances are stability and persistence in a wide variety of perfumed articles and perfume compositions, ease of manufacture, and intensity of aroma.

Woody, orrissey, melony, herbal, patchouli-like, green, fruity and camphoraceous notes are particularly desirable for many uses in conjunction with perfumes and perfumed compositions and articles.

Various nitriles not containing the tricycylene moiety have been described as being useful in altering the organoleptic characteristics of fragrances for use in conjunction with perfume compositions and perfumed articles.

Arctander, Perfume and Flavor Chemicals (Aroma Chemicals) 1969 contains the following teachings:

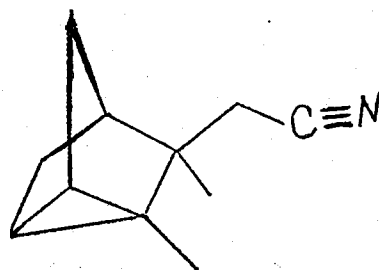
- i. At No. 1451, the perfume use of geranyl nitrile;
- ii. At No. 1439, the perfume use of geranyl isobutyronitrile;
- iii. At No. 641, the perfume use of cinnamyl nitrile;
- iv. At No. 764, the perfume use of beta(2,6,6-trimethyl-2-cyclohexenyl) vinyl cyanide
- v. At No. 1064, the perfume use of 2,2-dimethyl-3-(2,6,6-trimethyl-2-cyclohexen-1-yl)-propionitrile having either of the structures:



This material is described as having a "sweet and floral, rather pungent odor, with balsamic undertones". No such materials have been discovered, wherein the combination of woody, orrissey, melony, herbal, patchouli-like, green, fruity and camphoraceous notes exist.

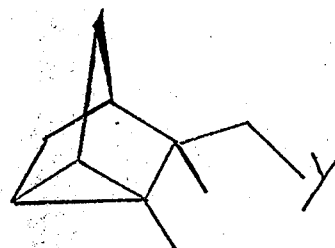
THE INVENTION

It has now been discovered that perfume formulations, perfumed materials and perfumed articles having one or more of woody, orrissey, melony, herbal, patchouli-like, green, fruity and camphoraceous notes may be provided by adding π -cyanotricyclene having the structure:



to perfume and fragrance-modifying materials or to materials to be fragranced (e.g., soaps or detergents).

The preparation of π -cyanotricyclene is carried out by reacting an alkali metal cyanide with a π -halo tricycylene having the generic formula:



wherein Y is a halogen selected from the group consisting of chloro, bromo and iodo. Examples of alkali metal cyanide useful in the reaction are sodium cyanide and potassium cyanide. The reaction is carried out in an inert solvent such as dimethyl sulfoxide at a temperature in the range of from 80°C up to 100°C; preferably 90°C. The mole ratio of alkali metal cyanide to π -halo tricycylene is from 10:1 up to 20:1 with a mole ratio of 15:1 being preferred.

It has been found that the π -cyanotricyclene of this invention possess one or more woody, orrissey, melony, herbal, patchouli-like, green, fruity and camphoraceous notes with good intensity and persistence. This fragrance quality particularly adapts the π -cyanotricyclene for incorporation into perfume compositions and fragrance-modifying compositions having desirable "Pine Needle Oil" aromas. It will be appreciated by those skilled in the art from the present disclosure that the fragrance character of the finished perfume compositions can be tailored to specific uses; as more fully described hereinafter.

The π -cyanotricyclene is an olfactory agent and can be incorporated into a wide variety of compositions which will be enhanced by any of the woody, orrissey, melony, herbal, patchouli-like, green, fruity and camphoraceous notes. The π -cyanotricyclene can be added to perfume compositions in its pure form or it can be added to mixtures of materials in fragrance-imparting compositions to provide a desired fragrance character to a finished perfume material. The perfume and fragrance compositions obtained according to this invention are suitable in a wide variety of perfumed articles and can also be used to enhance, modify or reinforce natural fragrance materials. It will thus be appreciated that the π -cyanotricyclene of this invention is useful as an olfactory agent and fragrance.

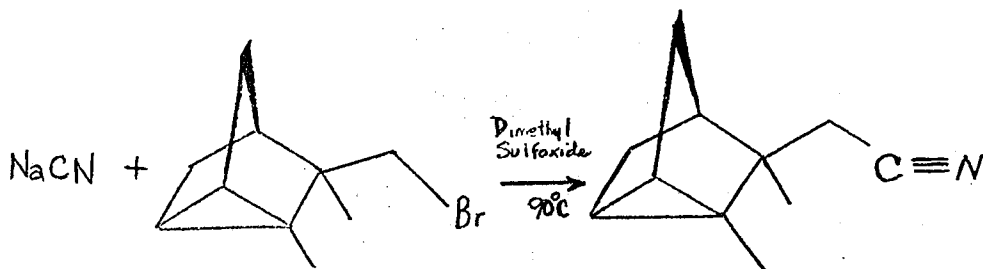
The term "perfume composition" is used herein to mean a mixture of compounds, including, for example, natural oils, synthetic oils, alcohols, aldehydes, ketones, esters, lactones, and frequently hydrocarbons

which are admixed so that the combined odors of the individual components produce a pleasant or desired fragrance. Such perfume compositions usually contain (a) the main note or the "bouquet" or foundation-stone of the composition; (b) modifiers which round-off and accompany the main note; (c) fixatives which

EXAMPLE I

Preparation of π -Cyanotricyclene

Reaction:



include odorous substances which lend a particular note to the perfume throughout all stages of evaporation; and substances which retard evaporation; and (d) top-notes which are usually low-boiling fresh-smelling materials. Such perfume compositions of this invention can be used in conjunction with carriers, vehicles, solvents, dispersants, emulsifiers, surface-active agents, aerosol propellants and the like.

In perfume compositions the individual components contribute their particular olfactory characteristics, but the overall effect of the perfume composition will be the sum of the effect of each ingredient. Thus, the π -cyanotricyclene of this invention can be used alone or in combination to alter the aroma characteristics of a perfume composition, for example, by highlighting or moderating the olfactory reaction contributed by another ingredient of the composition.

The amount of π -cyanotricyclene of this invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as much as 50% or as little as 0.6% by weight of mixtures or compounds of this invention, or even less can be used to impart one or more woody, orrissey, melony, herbal, patchouli-like, green, fruity and camphoraceous aromas to soaps, cosmetics, and other products. The amount employed will depend on considerations of cost, nature of the end product, the effect desired in the finished product, and the particular fragrance sought.

The π -cyanotricyclene disclosed herein can be used alone or in a fragrance-modifying composition, or in a perfume composition as olfactory components in detergents and soaps, space deodorants; perfumes; colognes; bath preparations such as bath oil, bath salts; hair preparations such as lacquers, brilliantines, pomades, and shampoos; cosmetic preparations such as creams, deodorants, hand lotions, sun screens; powders such as talcs, dusting powders, face powder and the like. When the π -cyanotricyclene of this invention are used in perfumed articles such as the foregoing, it can be used in amounts of 0.1 percent or lower. Generally, it is preferred not to use more than about 20 percent in the finished perfumed article, since the use of too much will tend to unbalance the total aroma and will needlessly raise the cost of the article.

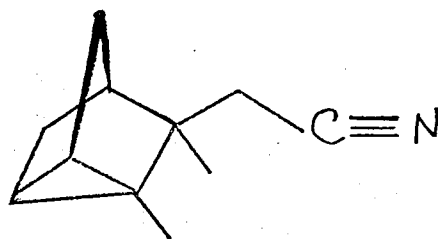
The following examples serve to illustrate embodiments of the invention as it is now preferred to practice it. It will be understood that these examples are illustrative and the invention is to be considered restricted thereto only as indicated in the appended claims.

Into a 500 ml 3-neck, round bottom flask equipped with condenser, thermometer, mechanical stirrer, hot water heating bath and N_2 purge is charged 200 cc distilled dimethyl sulfoxide. 21.6 g (0.1 moles) of (-)- π -bromotricyclene is then added into the 500 ml flask containing the 200 ml of dimethyl sulfoxide. While stirring and purging with nitrogen 77.6 g (1.58 moles) of sodium cyanide is then added. Heating by means of the hot water bath to 90°C is then effected, and the 90°C temperature is maintained for 22 hours. The reaction mass is then cooled to 40°C (below which temperature it becomes solidified) and 200 ml of water is added thereto. The aqueous phase is then extracted with five 100 ml portions of petroleum ether. The combined petroleum ether extracts are then washed with three 50 ml portions of saturated sodium chloride solution and dried over anhydrous $MgSO_4$. The dried extract is filtered and the solvents are evaporated yielding 21.2 g of crude product.

The crude product is distilled on a 2 inch rush-over column and collected three fractions. While distilling the condenser has to be heated as the pure nitrile solidifies.

Distillation Data:				
Fraction No.	Vapor Temp.	Liquid Temp.	Weight of Fraction	Pressure
1	30-52°C	60-65°C	0.1 g	0.15 mm Hg
2	55	70	1.7	0.15
3	70	90	9.0	0.10

NMR, mass spectral and IR analyses confirm that fractions 1 and 2 consist essentially of π -cyanotricyclene having the structure:



The mass spectral analysis of π -cyanotricyclene in order of decreasing intensity is as follows:

$m/e = 93, 121, 39, 27, 41.$

5

The NMR spectrum of π -cyanotricyclene is set forth in FIG. 1 and its IR spectrum is set forth in FIG. 2.

EXAMPLE II

Pine-Needle Perfume Formulation

The following mixture is prepared:

Ingredient	Parts by Weight
π -Cyanotricyclene (prepared according to the process of Example I)	50
Terpentine Gum Oil	100
Limenone	50
Isobornyl Acetate	100
Orange Oil	25
Gum Camphor	20
Lauryl Aldehyde	3
Borneol	50
Terpineol	15
Palatone (3-hydroxy-2-methyl-4-pyrone)	3

The π -cyanotricyclene imparts a green, melony, herbaceous character so necessary for pine-needle oil.

EXAMPLE III

Preparation of Soap Composition

One hundred grams of soap chips are mixed with one gram of the perfume composition of Example II until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent Pine Needle character with a green, melony, herbaceous character.

EXAMPLE IV

Preparation of a Detergent Composition

A total of 100 grams of a detergent powder is mixed with 0.15 grams of the perfume composition of Example II until a substantially homogeneous composition is obtained. This composition has an excellent Pine Needle oil odor with a green, melony, herbaceous character.

EXAMPLE V

Preparation of a Cosmetic Powder Composition

A cosmetic powder is prepared by mixing in a ball mill 100 grams of talcum powder with 0.25 grams of π -cyanotricyclene produced according to Example I. It has an excellent woody, camphoraceous, orrissey aroma.

EXAMPLE VI

Perfumed Liquid Detergent

Concentrated liquid detergents with a woody, camphoraceous and orrissey odor are prepared containing 0.10 percent, 0.15 percent and 0.20 percent of π -cyanotricyclene. They are prepared by adding and homogeneously mixing the appropriate quantity of π -cyanotricyclene in the liquid detergent. The detergents all possess a woody, camphoraceous, orrissey fragrance, the intensity increasing with greater concentration of π -cyanotricyclene.

EXAMPLE VII

Preparation of a Cologne and Handkerchief Perfume

π -Cyanotricyclene is incorporated in a cologne at a concentration of 2.5 percent in 85 percent aqueous

6

ethanol; and into a handkerchief perfume at a concentration of 20 percent (in 95 percent aqueous ethanol). A distinct and definite strong woody, camphoraceous, orrissey fragrance is imparted to the cologne and to the handkerchief perfume.

EXAMPLE VIII

The composition of Example II is incorporated in a cologne at a concentration of 2.5 percent in 85 percent aqueous ethanol; and into a handkerchief perfume at a concentration of 20 percent aqueous ethanol). The use of the π -cyanotricyclene in the composition of Example II affords a distinct and definite strong Pine Needle type perfume aroma having a green, melony and herbaceous character to the handkerchief perfume and cologne.

EXAMPLE IX

Preparation of Soap Composition

One hundred grams of soap chips are mixed with one gram of the π -cyanotricyclene of Example I until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent woody-patchouli character with camphoraceous, orrissey and fruity notes.

EXAMPLE X

Preparation of a Detergent Composition

A total of 100 grams of a detergent powder is mixed with 0.15 grams of the π -cyanotricyclene of Example I until a substantially homogeneous composition is obtained. This composition has an excellent woody, patchouli odor with camphoraceous, orrissey and fruity notes.

EXAMPLE XI

Preparation of a Cosmetic Powder Composition

A cosmetic powder is prepared by mixing in a ball mill, 100 grams of talcum powder with 0.25 grams of the composition of Example II. It has an excellent Pine Needle Oil character.

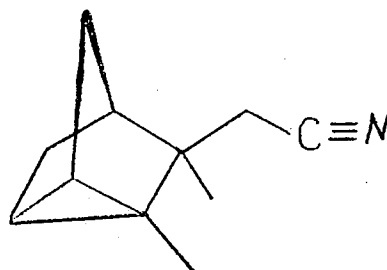
EXAMPLE XII

Perfumed Liquid Detergent

Concentrated liquid detergents with Pine Needle Oil fragrances are prepared containing 0.5 percent, 0.7 percent and 0.9 percent of the composition of Example II. They are prepared by adding and homogeneously mixing the appropriate quantity of the composition of Example II in the liquid detergent. The detergents all possess a Pine Needle Oil fragrance with green, melony and herbaceous notes, the intensity increasing with greater concentration of the composition of Example II.

What is claimed is:

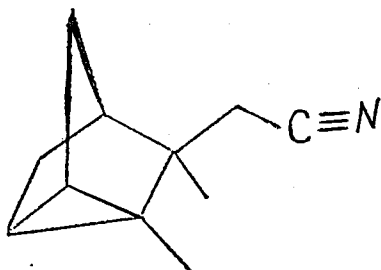
1. A perfume composition comprising π -cyanotricyclene having the structure:



7

and at least one adjuvant selected from the group consisting of natural perfume oils, synthetic perfume oils, alcohols, aldehydes, ketones, esters and lactones.

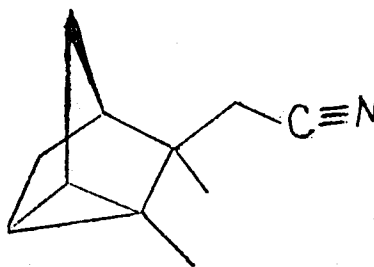
2. A perfumed article comprising π -cyanotricyclene 5 having the structure:



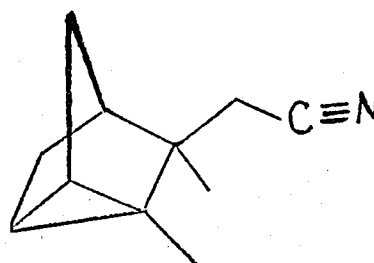
and a detergent, soap, bath preparation, hair preparation, cosmetic preparation or powder.

3. A process for preparing a perfumed composition comprising the step of admixing a composition of matter with a fragrance-imparting amount of π -cyanotricyclene having the structure:

8



4. A cologne composition comprising π -cyanotricyclene having the structure:



and ethanol and water.

* * * * *