

[54] **FLAVORED TOBACCO PRODUCT**

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[58] Field of Search 131/143, 144, 17, 2, 15; 426/65

[56]

References Cited

UNITED STATES PATENTS

3,316,919 5/1967 Green et al. 131/143

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[57]

ABSTRACT

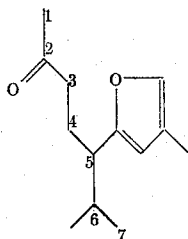
A novel flavoring composition is disclosed which is useful in flavoring both tobacco and tobacco substitute materials. The compound, 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one, is added in an amount of from 1 to 500 p.p.m. by weight of the tobacco product.

1 Claim, No Drawings

FLAVORED TOBACCO PRODUCT

DESCRIPTION OF THE INVENTION

The present invention relates to a novel compound of formula



and to a process for its preparation. The said compound is defined as 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one.

BACKGROUND OF THE INVENTION

It is well known that the tobacco used, for example, for the manufacture of cigarettes comprises a mixture of different types, to give the characteristic flavour and aroma desired in the smoke produced. Thus, cigarettes currently manufactured usually contain mixtures of Virginia, Maryland or Kentucky tobacco in combination with oriental or Turkish tobacco.

The respective proportions of the various types of tobacco are varied in order to obtain the particular flavour and aroma desired. It is also common practice, to employ flavouring substances and humectants as additives to these tobacco mixtures to further enhance the organoleptic properties thereof.

Accordingly, it is an object of the present invention to provide a tobacco or tobacco product having added thereto a small but flavour-modifying quantity of a flavour ingredient, the 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one.

Equally, we have surprisingly found that in view of its specific organoleptic properties, the said compound may find a useful industrial application for the aromatisation of a great variety of materials, namely of foodstuffs and beverages. The said compound represents also a useful perfuming ingredient.

We have found that by adding to a tobacco base (which may be natural tobacco or a tobacco substitute of natural or synthetic origin) These properties are particularly developed on smoking. However, it is to be appreciated that definition or characterisation of flavour or aroma in the tobacco art is in many instances purely subjective and different smokers may define the same flavour or effect quite differently.

5-(4-methyl-2-furyl)-6-methyl-heptan-2-one in its pure form or in admixture with other flavouring ingredients, may be employed in a variety of forms. The chemical nature, solubility and stability determine the form in which the given compound or composition thereof is to be employed. It is preferable, however, to utilize the said compound or composition in the form of solutions thereof.

The additive can be added at any step in the course of the treatment of the tobacco but it is preferably added after aging, curing and shredding and before the tobacco is formed into cigarettes or other products.

A convenient method for flavouring tobacco consists in spraying the tobacco with an alcoholic solution of the compound or flavouring mixture. Combination of

solvents such as alcohol and propylene glycol may also be used.

The proportions of the new compounds to be used in said compositions or in accordance with the process of the present invention can vary within wide limits. Said proportions depend particularly on the specific organoleptic effects it is desired to achieve and on the origin of the tobacco products to which the mentioned flavouring ingredients are added.

For instance, interesting flavouring effects can be achieved with amounts ranging from 1 to 500 ppm, preferentially comprised between about 10 and 200 ppm, more particularly between about 10 and 20 ppm, based on the weight of the product flavoured. When the compound of formula I is used for the flavouring of foodstuffs, feedstuffs, beverages or pharmaceutical preparations, analogous proportions may be employed.

When the compound of the invention is used for the preparation of artificial flavour compositions, its proportions may be increased up to about 80 percent by weight of the composition.

When the compound of the invention is used as perfuming ingredient its proportions in the perfume compositions or perfumed products to which it is added may equally be comprised in a wide range. Thus, interesting odoriferous effects may be achieved by amounts of from about 1 percent to about 10 percent of the total weight of the composition.

In all cases, the ranges given above may be varied, depending upon the specific odoriferous or flavouring effect it is desired to achieve.

The 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one is a compound of natural origin. Said compound has been in fact isolated now for the first time from a natural essential oil. The essential oil has been obtained by extraction with a volatile solvent from the aqueous distillate collected by vapour distillation of Burley tobacco upon previous acidification of the said distillate to ca. pH 4.

The isolation procedure mentioned above is particularly complex and uneconomical as the essential oil is obtained with a yield not higher than 0.03 percent by weight of the total tobacco treated. In fact, after the recovery of the essential oil the isolation process consisted in a preliminary separation by fractional distillation under reduced pressure, whereupon the less volatile fractions [B. p. >35°C/0.001 Torr] were subjected to several distillations by means of high fractionating power columns.

Finally, the isolation of the desired ketone of formula I, has required the use of specific techniques wherein there was employed preparative vapour phase chromatography (pvpc) utilizing stationary phases of contrasted polarity.

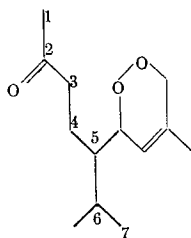
The 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one is merely a minor constituent of the essential oil. Said compound has been detected in a concentration of ca. 0.05 percent. In its pure state this compound possesses an unprecedented original flavouring and perfuming notes. It can in fact develop or simply enhance a variety of notes such as fruity and flowery notes. These organoleptic characters are particularly suitable for the aromatisation of infusions or decoctions such as tea, camomile, lime tea or verbena for example. When the compound of the invention is used as perfuming ingredient, it can develop very interesting notes with a herbal character.

Its power and tenacity are particularly appreciated in the art, particularly in view of the fact that the above described organoleptic characters are stable and perfectly reproducible. These properties belong specifically to the pure compound, whereas on the contrary, the aroma and odour of the natural essential oil varies in accordance with the origin of the tobacco which has been used as base material for the extraction; the extraction methods chosen and the purity of the essential oil recovered.

As a consequence, in view of its flavouring and perfuming properties, ketone I possesses a clearly distinct field of application, said application being also wider than of the natural essential oil.

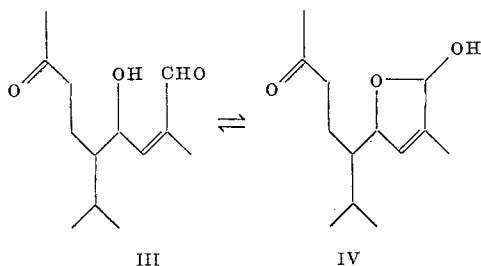
By means of an original, industrial and economic process, it is now possible to put to the disposal of the perfumers and flavourists a practically pure 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one. The difficulties due to the supply and storage of the tobacco material required for the extraction of the essential oil are thus avoided.

According to the invention, 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one is prepared by a process which comprises treating a cyclic peroxide of formula



with a basic agent and dehydrating then the product thus obtained. Suitable basic agents include mineral or organic bases, such as, e.g., alkali metal hydroxides or alkoxides, or secondary or tertiary amines such as dimethylamine, triethylamine, pyridine, α -, β - or γ -picoline, piperidine or morpholine.

Basic aluminium oxide may equally be employed. In this latter case, the conversion is preferably effected by absorption, on a column filled up with the basic agent, of a solution of compound II in an inert organic solvent. Suitable organic solvent include an aromatic hydrocarbon such as benzene or toluene. The final product is obtained by subsequent elution by means of a mixture of alcohol and ether, preferably a mixture of methanol or ethanol and diethyl ether. It is likely that the treatment with basic agent leads to the formation of an intermediate of formula III. Said compound may be in equilibrium with a hydroxy-dihydrofuran of formula IV as indicated below:



Said conversion is in agreement with the mechanism originally suggested in J. Am. Chem. Soc. 73, 880 (1951).

The dehydration of the obtained compound, or of the mixture of the obtained compounds of formula III and IV, can be carried out in accordance with the techniques conventional in the art.

Thus, the product directly issued from the previous treatment can be treated with an acid or basic dehydrating agent in order to give the furanic compound of formula I. This dehydration can also be effected by means of heat. In order to promote such a reaction it is necessary to operate at temperatures comprised between about 20°C. and about 250°C. By operating at room temperature it has been possible to observe the formation of an appreciable amount of the final product. However, in order to achieve a rapid and complete dehydration it is preferred to operate at temperature higher than the room temperature, preferably at temperatures comprised in the vicinity of 200°C.

Compound II, used as starting material in the process of the invention, can be prepared by oxidation by means of singlet oxygen of solanone, also known under the name of 5-iso-propyl-8-methyl-nona-6,8-dien-2-one. This compound can be synthesized according to known methods [cf. e.g.: J. Org. Chem. 30, 2918 (1965)]. The oxidation by means of singlet oxygen can be promoted by means of a sensitized photooxygenation. Suitable sensitizers include conventional dyestuffs such as, e.g., porphyrines, methylene blue, eosin, chlorophyll, Rose-Bengal or xanthene [cf.: Liebig's Ann. Chem. 674, 93 (1964); Angew. Chem. 69, 579 (1957)]. Said photooxygenation can be carried out at temperatures near to or higher than 0°C, preferably at room temperature.

The photooxygenation can be effected in a protic medium, for instance in an alcoholic solution in methanol or ethanol, or in a solution of an aromatic hydrocarbon, such as benzene or toluene, an aliphatic hydrocarbon, such as n-hexane or cyclohexane, or an ether such as dioxane or tetrahydrofuran.

Singlet oxygen can be obtained in accordance with one of the known chemical methods [see for example: C. S. Foote, Accounts of Chem. Research 1, 104 (1968)].

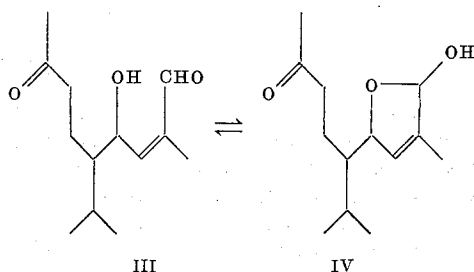
The invention will be better illustrated by one of the following examples wherein the temperatures are given in degrees centigrade and the abbreviations have the meaning conventional in the art.

EXAMPLE 1

5-(4-Methyl-2-furyl)-6-methyl-heptan-2-one

a 300 mg of peroxide directly obtained by actinic irradiation and oxidation of solanone in accordance with the method indicated in paragraph b) in 3 ml of dry benzene have been absorbed on a column containing 10 g of basic aluminium oxide (WO-ELM; activity I). After 2 hr at 20° the product has been eluted with 50 ml of a 4:1 mixture of ether and methanol. On drying and evaporation of the volatile portions they were obtained 264 ml (yield 88 percent) of a product probably containing a compound of structure III, said compound being in equilibrium with its cyclic derivative of structure IV.

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By injection of the product thus obtained in a vapour phase chromatograph, separation on a CARBOWAX column (5 percent; 2,5 m., 200°) and condensation of the formed products, there was obtained the desired product with an yield of ca. 80 percent by weight of the product injected in the apparatus.

IR: 3100, 1715, 1610, 1540, 1360, 1035 and 800 cm^{-1}

NMR (CDCl_3) at 90 MHz: 0.80 (3H, d, $J=7$ cps); 0.92 (3H, d, $J=7$ cps); 2.00 (3H, s); 2.07 (3H, s); 2.31 (2H, t, $J=7$ cps); 5.86 (1H, s) and 7.07 (1H, m) δ ppm

UV: $\lambda_{\text{max}}^{\text{EtOH}} = 220 \text{ nm}$;

MS: $M^+ = 208$; m/e : 150, 43.

The peroxide used as starting material in the process described hereinabove can be prepared as follows:

b. 1 g of solanone in 200 ml methanol have been irradiated in the presence of 180 mg of Rose Bengal at 20° in a vessel destined to photochemical reactions by means of a mercury vapour lamp of 125 W (Type PHILIPS HPK). During the irradiation the solution was saturated with dry oxygen which was bubbled through at a rate of 80 ml/min.

The course of the reaction was followed by a regular control by means of ultraviolet spectroscopy by observing the shortening of the intensity of the absorption band at 230 nm ($\epsilon=27,300$) of solanone.

After 40 hr irradiation the solution was concentrated under reduced pressure at low temperature and the thus obtained residue was taken up by ether. By the usual treatments of washing with water, separation and drying, the ethereal phase gave on evaporation of the volatile portions a product which, by purification by means of col-

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umn chromatography on silica gel (20 g; elution with a mixture of benzene and ethyl acetate 95:5), gave 320 mg of the desired peroxide of formula II.

IR: 1710, 1360, 1160 cm^{-1} ;

NMR (CCl_4):

0.75–1.10 (6H, m); 1.15–1.90 (4H, m); 1.73 (3H, s); 2.05 (3H, s); 2.20–2.70 (2H, m); 4.15–4.70 (3H, m); 5.60 (1H, s, broad band) δ ppm.

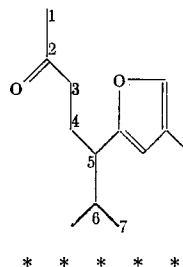
EXAMPLE 2

1 g of a 1 percent solution of 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one in 95 percent ethanol was sprayed onto 100 g of a tobacco mixture of the "american blend" type. The tobacco thus flavoured was then used for the manufacture of "test" cigarettes the smoke of which was subjected to an organoleptic evaluation by a panel of flavour experts. These latter unanimously declared that the smoke of the "test" cigarettes presented a typical character and a pleasant aroma of dry leaves when compared with the smoke of "control" cigarettes the tobacco of which was previously treated with 95 percent ethanol. The tobacco note of the flavoured cigarettes was also enhanced. The smoke of these cigarettes presented moreover a slightly fruity and flowery character.

Analogous results were observed by using solutions containing a higher proportion of the same ingredient. In this latter case, however, the effect was more powerful but somewhat unbalanced.

I claim:

1. A tobacco product selected from the group consisting essentially of tobacco and tobacco substitutes which has added thereto of between about 1 to 500 ppm by weight of the flavouring compound consisting essentially of 5-(4-methyl-2-furyl)-6-methyl-heptan-2-one which manifests the following formula:



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