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3,381,691

TOBACCO PRODUCT

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16 Claims. (Cl. 131-17)

This invention relates to a tobacco product and has for an object the provision of a composition and process for improving the flavor and aroma of tobacco and tobacco smoke.

It is well known in the tobacco art that the flavor and aroma of the tobacco product and the smoke from the tobacco are very important considerations in so far as the ultimate consumer is concerned. Considerable efforts are exerted by the manufacturers of tobacco products to provide a product that will be acceptable to the consumer, particularly as regards flavor and aroma characteristics. It has been the common practice in the tobacco industry to prepare blends of domestic and oriental tobaccos in order to provide smoking tobacco which has a pleasing flavor and aroma before and during smoking. However, such a procedure is costly and may at times become prohibitive in the event that certain types of tobacco may be in short supply. Accordingly, it is a further object of this invention to provide a new class of additive materials which when applied to the tobacco products improve and enhance the flavor and aroma of these products and the smoke emitted therefrom, thereby increasing or enhancing the pleasure and other values that may be derived by the consumer from the use of these products.

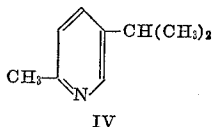
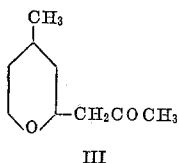
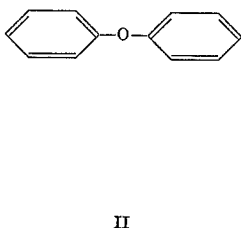
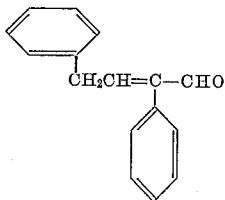
A further object of this invention is the provision of a process for enhancing or otherwise improving the flavor, aroma and other qualities of certain domestic, oriental, reconstituted or synthetic tobaccos which may be deficient in said flavor or aroma or other qualities.

An additional object of this invention is to provide a process of preparing a smoking tobacco or product which when smoked has an enhanced flavor or aroma.

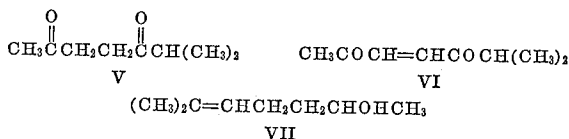
A still further object of this invention is the provision of smoking products, such as cigarettes, cigars or pipe tobacco, and a process for forming same whereby the flavor and aroma before and during smoking are improved or enhanced.

Further and additional objects will appear from the following description and the appended claims.

In accordance with one embodiment of this invention, a tobacco product is provided to which has been added or which has been treated with a small amount of a compound selected from the group having the formulae:



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EXAMPLE 1

A. Synthesis and properties of 2,4-diphenylcrotonaldehyde (Formula I)

This compound was prepared according to the procedure of W. Triebs and K. Krumbholz, Chem. Ber., 85, 1116-19 (1952) by the dropwise addition of 50 grams phenylacetaldehyde to 2 milliliters of ethanol containing 90 milligrams of acetic acid and 0.125 gram of piperidine, yielding 18.8 grams of 2,4-diphenylcrotonaldehyde, boiling point 202-5°/1 millimeter, nuclear magnetic resonance spectrum:  $\tau=6.32(2d)$ ; 3.15(1); 2.73(10); and 0.33(1).

EXAMPLE 2

The compound of Formula II is the commercially available chemical diphenylether having a melting point of 26-27° and a nuclear magnetic resonance spectrum:  $\tau=2.70(10)$ .

EXAMPLE 3

A. Synthesis and Properties of 2-acetyl-4-methyltetrahydropyran (Formula III)

(1) Preparation of 2-hydroxy-4-methyltetrahydropyran.—To a solution of 20 grams of  $\beta$ -methyl- $\delta$ -valerolactone, commercially available, in 50 milliliters of absolute ether was added dropwise a solution of 1.67 grams of lithium aluminum hydride in 50 milliliters of ether. After refluxing for an hour, the solution was hydrolyzed with water and the ether layer was separated from the aqueous layer. The aqueous layer was extracted twice more with ether and the combined ether layers were dried and concentrated, yielding 11.3 grams of 2-hydroxy-4-methyltetrahydropyran.

(2) 2-acetyl-4-methyltetrahydropyran.—2-hydroxy-4-methyltetrahydropyran (11.3 grams) was added dropwise to a stirred solution of 36 milliliters of acetone, 36 milliliters of water and 3 grams of a 30% sodium hydroxide solution. After stirring for six hours, the solution was allowed to stand 16 hours and then was neutralized with 10% acetic acid. The aqueous layer was extracted several times with ether and the residue from the ether layers was distilled, yielding 7.3 grams of 2-acetyl-4-methyltetrahydropyran, boiling point 56-63° C./1 millimeter; nuclear magnetic resonance spectrum:  $\tau=9.06(3)$ ; 7.86(3); 7.53(2); and 6.37(2).

EXAMPLE 4

A. Synthesis and Properties of 2-methyl-5-isopropylpyridine (Formula IV)

Ethyl 6-methylnicotinate, boiling point 113-16°/11 millimeters was prepared according to the method of P. A. Plattner, W. Keller and A. Boller, Helv. Chim. Acta., 37, 1379-92 (1954). The ester, 5.5 grams in 25 milliliters of ether, was added dropwise to 40 milliliters of methylmagnesium bromide, 3 molar, in ethyl ether. After the addition, the mixture was refluxed two hours and decomposed with potassium hydroxide. The resulting layers were separated. The water layer was extracted with ether, and the ether extract was combined with the organic layer, which was then dried over sodium sulphate. Removal of the solvent in vacuo yielded 4 grams of crude 6-methylpyridine-5-dimethylcarbinol.

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The crude carbinol was mixed with 35 grams of hydriotic acid and one gram of red phosphorous. The mixture was boiled 10 hours and then filtered. Two grams of zinc dust were added to the filtrate. After four hours, 10% potassium hydroxide was added and the mixture was extracted with ether. The ether layer was dried over sodium sulphate and the ether removed in vacuo. The residue was distilled, yielding 1.5 grams of 2-methyl-5-isopropylpyridine, boiling point 73-4° C./15 millimeters; nuclear magnetic resonance spectrum:  $\tau=8.80(3)$ ; 8.70(3); 7.52(3); 7.06(1); 2.60(1); and 1.65(1).

#### EXAMPLE 5

##### A. Synthesis and properties of 6-methyl-2,5-heptanedione (Formula V)

in a 500-milliliter 3-necked flask equipped with a magnetic stirring bar, reflux condenser, nitrogen inlet tube and a pressure-equalizing addition funnel. Isopropyl lithium (160 milliliters, 1.33 molar in pentane) was transferred to the addition funnel under nitrogen pressure and added dropwise over 1.5 hours. After an additional hour of stirring, water was slowly and cautiously added. The organic layer that formed was separated and the solvent removed in vacuo. The residue was mixed with 100 milliliters of 10% sulphuric acid and 60 milliliters of ethanol. After refluxing ½ hour, the reaction mixture was diluted with water and extracted with ether. The ether extract was dried, the ether removed in vacuo and the residue was distilled, yielding 14 grams of 6-methyl-2,5-heptanedione, boiling point 88-89°/15 millimeters, nuclear magnetic resonance spectrum:  $\tau=9.0(3)$ ; 8.88(3); 7.90(3); and 7.40(5).

#### EXAMPLE 6

##### A. Synthesis and properties of 6-methyl-3-heptene-2,5-dione (Formula VI)

A mixture of 10 grams of 6-methyl-2,5-heptanedione, 6 grams of selenium dioxide, and 200 milliliters of water was warmed at 75° for 12 hours. The mixture was filtered, and the filtrate was saturated with ammonium sulphate and extracted with ether. The residue, after removing the ether in vacuo, was distilled, yielding 5 grams of 6-methyl-3-heptene-2,5-dione, boiling point 98-100° C./2 millimeters; nuclear magnetic resonance spectrum:  $\tau=8.90(3)$ ; 8.78(3); 7.64(3); 7.10(1); and 3.13(2).

#### EXAMPLE 7

##### A. 6-methyl-5-hepten-2-ol (Formula VII)

The compound 6-methyl-5-hepten-2-ol is commercially available and has the following properties: boiling point 80° C./25 millimeters; infrared spectrum:  $\nu=3300$ , 1620, and 1115  $\text{cm}^{-1}$ ; nuclear magnetic resonance spectrum:  $\tau=4.83(1, \text{triplet})$ , 6.15 (1, quadruplet), 7.92(2), 8.30(3), 8.37(3) and 8.83 (3, doublet); mass spectrum: parent peak at 128 mass units.

It has been found that the tobacco additives of the invention when incorporated into tobacco products impart a flavor and arom both before and during smoking which many smokers consider to be desirable in smoking products. However, it is pointed out that the methods for defining or characterizing the quality of a flavor or aroma in the tobacco art are almost purely subjective and different smokers may define the same flavor quite differently. Also, the compounds included within the broad scope of this invention may impart different flavors or aromas depending upon the substituents therein. Thus, the compounds comprehended by this invention, by subjective tests, impart characteristic flavors which are desirable in tobacco products and the smoke therefrom even though the exact character thereof cannot be described on the basis of known standards. The tobacco additive of Example 1 imparts a sweet flowery aroma or flavor which is reminiscent of geraniums which many smokers con-

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sider to be desirable in a tobacco product. The tobacco additive of Example 2 imparts an aroma which some characterize as similar to camphor-menthol; the tobacco additive of Example 3 has a mild rose odor and imparts a banana-spicy aroma; the tobacco additive of Example 4 has an odor reminiscent of sweet potatoes; the compounds of Examples 5 and 6 impart a sweet taste; and the tobacco additive of Example 7 has a camphor note.

In accordance with this invention, an above indicated compound or a mixture of compounds is added to tobacco or applied to a smoking article or its component parts in amounts of about 0.0001 to 2.0 percent by weight of the product. However, the amount used will depend upon the amount of flavor and aroma desired and the particular compound or mixture thereof that is used. The additive may be incorporated at any step in the treatment of the tobacco but is preferably added after aging, curing and shredding and before the tobacco is formed into cigarettes. Likewise, it will be apparent that only a portion of the tobacco need be treated and the thus treated tobacco may be blended with other tobaccos before the cigarettes or other smoking articles are formed. In such case the tobacco treated may have the additive in excess of the amounts above indicated so that when blended with other tobaccos the final product will have the percentage within the indicated range.

In accordance with one specific embodiment of this invention, an aged, flue-cured and shredded tobacco is sprayed with a 1% ethyl alcohol solution of 2,4-diphenylcrotonaldehyde in an amount to provide a tobacco containing about 0.25 percent by weight of the additive on a dry basis. Thereafter the alcohol is removed by evaporation and the tobacco is manufactured into cigarettes by the usual techniques. It has been found that the cigarette when prepared as indicated has a desired and pleasing flavor, an aroma which to some people is reminiscent of geranium and is detectable and pleasing in the main and side smoke streams when the cigarette is smoked.

The additives falling within the scope of this invention may be applied to the tobacco by spraying, dipping or otherwise, utilizing suitable suspensions or solutions of the additive. Thus water or volatile organic solvents, such as alcohol, ether, acetone, volatile hydrocarbons and the like, may be used as the carrying medium for the additive while it is being applied to the tobacco. Also, other flavor- and aroma-producing additives, such as those disclosed in United States Patents Nos. 2,766,145, 2,905,575, 2,905,576, 2,978,365 and 3,041,211 may be incorporated into the tobacco with the additive of this invention.

While this invention is principally useful in the manufacture of cigarette tobacco, it is also suitable for use in connection with the manufacture of pipe tobacco, cigars or other tobacco products. Furthermore, the compounds may be added to certain tobacco substitutes of natural or synthetic origin and by the term "tobacco" as used throughout this specification is meant any composition intended for human consumption by smoking or otherwise, whether composed of tobacco plant parts or substitute materials or both.

Also, the invention has been particularly described with reference to the addition of the compounds directly to tobacco. However, it will be apparent that the compound may be applied to the paper of the cigarette or to the wrapper of a cigar. Also, it may be incorporated into the filter tip, the packaging material or the seam paste employed for gluing the cigarette paper. Thus a tobacco product is provided which includes the specified additives and tobacco although in every instance the compound need not be admixed with the tobacco as above specifically described.

While several particular embodiments of this invention are shown above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims, to cover any such modifica-

tions as fall within the true spirit and scope of this invention.

We claim:

1. A tobacco product having added thereto an amount sufficient to alter the flavor or aroma of the tobacco product of a compound selected from the group 2,4-diphenylcrotonaldehyde, diphenylether, 2-acetyl-4-methyltetrahydropyran, 2-methyl-5-isopropylpyridine, 6-methyl-2,5-heptanedione, 6-methyl-3-heptene-2,5-dione, and 6-methyl-5-hepten-2-ol.
2. The tobacco product recited in claim 1 wherein the amount of the flavoring compound is between about 0.0001 and 2.0 percent by weight of the product.
3. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of 2,4-diphenylcrotonaldehyde.
4. The tobacco product recited in claim 3 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.
5. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of diphenylether.
6. The tobacco product recited in claim 5 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.
7. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of 2-acetyl-4-methyltetrahydropyran.
8. The tobacco product recited in claim 7 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.

9. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of 2-methyl-5-isopropylpyridine.

10. The tobacco product recited in claim 9 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.

11. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of 6-methyl-2,5-heptanedione.

12. The tobacco product recited in claim 11 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.

13. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of 6-methyl-3-heptene-2,5-dione.

14. The tobacco product recited in claim 13 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.

15. A tobacco product having added thereto a small amount sufficient to improve the flavor thereof of 6-methyl-5-hepten-2-ol.

16. The tobacco product recited in claim 15 wherein the flavoring additive is present in an amount between about 0.0001 and 2.0 percent by weight of the product.

#### References Cited

#### UNITED STATES PATENTS

2,766,149 10/1956 Rowland ----- 13-17

SAMUEL KOREN, *Primary Examiner.*

D. J. DONOHUE, *Assistant Examiner.*

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,381,691

May 7, 1968

Joseph N. Schumacher et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 11, after "7.06(1);" insert -- 2.96(1) -- ;  
line 16, cancel "in a 500-ml, liter 3-necked flask equipped  
with a mag" and insert -- Ethyl levulinate ethylene glycol  
ketal (35 grams) was --; line 60, "arom" should read -- aroma --.  
Column 4, line 44, cancel the period and insert a comma. Column  
6, line 28, "13-17" should read -- 131-17 --.

Signed and sealed this 23rd day of September 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents