United States Patent [19]

Vinals et al.

[11] **3,861,403**

[45] **Jan. 21, 1975**

[54] **NOVEL TOBACCO PRODUCT COMPRISING ONE OR MORE ALPHA-PYRONES**

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[22] Filed: **May 20, 1974**

[21] Appl. No.: **471,785**

[52] **U.S. Cl.** ..... **131/17 R,** 131/144, 131/15 R

[51] **Int. Cl.** **A24b 15/00**

[58] **Field of Search** 131/2, 15, 17, 144, 9

[56] **References Cited**

UNITED STATES PATENTS

3,380,457 4/1968 Schumacher et al. ..... 131/17 R

FOREIGN PATENTS OR APPLICATIONS

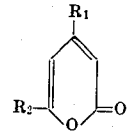
748,645 5/1956 Great Britain ..... 131/144 X

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[57] **ABSTRACT**

Described is a tobacco product having added thereto an amount sufficient to alter the flavor or aroma of the tobacco product particularly on smoking, of one or more alpha-pyrone compounds having the generic structure:



wherein R_1 is methyl or hydrogen, and R_2 is C_3–C_5 alkyl; processes for producing such tobacco products; and flavor formulations for use in conjunction with tobacco products containing one or more of such alpha-pyrones.

12 Claims, No Drawings

NOVEL TOBACCO PRODUCT COMPRISING ONE OR MORE ALPHA-PYRONES

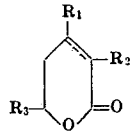
BACKGROUND OF THE INVENTION

This invention relates to novel tobacco products, and has for an object the provision of a composition 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 insofar as the ultimate consumer is concerned. Considerable efforts have been and are being 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, there has been considerable work relating to substances which can be used to impart flavors to various tobacco blends. These substances are used to supplement natural materials some of which, as stated above, may be in short supply, and to provide more uniform properties to the finished product.

Sweet, aromatic, warm, spicy, maple-like, fruity, coumarin-like, vanillin-like, lactone, lovage-like, celery-like and nut-like notes are particularly desirable for many uses concerning the flavoring of tobacco products; both prior to and on smoking.

Schumacher et al., U.S. Pat. No. 3,380,457 issued on Apr. 30, 1958 described an improved tobacco product containing a lactone compound having the generic structure:



wherein one or more of R_1, R_2 and R_3 are hydrogen or alkyl and wherein the dashed line represents a single bond or a double bond. Schumacher et al. states that an aroma and flavor which is reminiscent of coconut may be imparted by the use of 3-isopropyl-delta-valerolactone as a tobacco additive; or by the use of 5-hydroxy-3-isopropyl-2-pentenoic acid delta lactone, as a tobacco additive; or a spicy note may be imparted by the use of 5-hydroxy-2-isopropylhexanoic acid delta lactone, as a tobacco additive; or a spicy apple note may be imparted by the use of beta-methyl-delta valerolactone as a tobacco additive.

Various alpha pyrones have been described as being useful in altering the organoleptic characteristics of flavors for foodstuffs as well as fragrances for use in conjunction with perfumed articles.

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

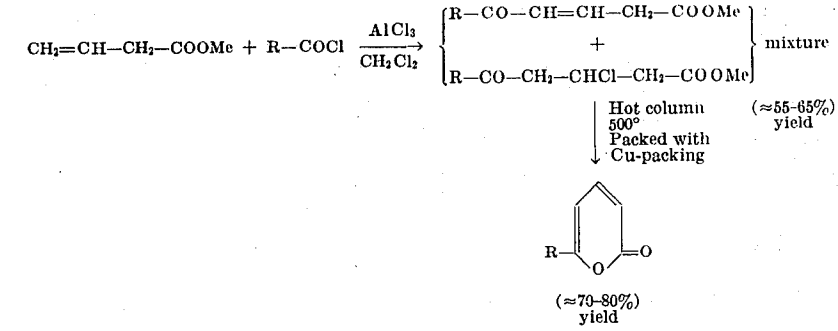
(i) At No. 1347, the flavor and perfume use of 5-ethyl-alpha pyrone;
(ii) At No. 2230, the flavor and perfume use of 5-methyl-alpha pyrone;
(iii) At No. 2781, the perfume use of alpha pyrone.

Taylor et al. British Patent 748,645 discloses at page 7, lines 105 and 106 the use in butter flavors of the lactones of unsaturated delta hydroxy acids. Sevenants, *J.Food Sci.*, 1971, 36 (3), 536 discloses the occurence of 6-pentyl-alpha-pyrone in peach aroma. Nobuhara, *Agr.Biol.Chem.* 1969, 33, No. 9, 1264–9 (Title: "Synthesis of Unsaturated Lactones/III: Flavorous Nature of Some delta-Lactones having the Double Bond at Various Sites") indicates the waxey, butter-cake flavor of 6-pentyl-alpha-pyrone at page 1267, col. 1. In addition, the flavor attributes of alpha-pyrones, in general, are discussed by Nobuhara.

Methods for the preparation of the alpha-pyrones found to be useful in our invention are disclosed as follows:

(i) Lohaus et al., Chemische Berichte, 100, 658 (1967);
(ii) Wiley et al., J.Org.Chem., 22, 1257–9, (1957);
(iii) Belgian Patent 643,891, Aug. 17, 1964;
(iv) Nobuhara, Agr.Biol.Chem. 1969 33(9), 1264–9;
(v) Pettit et al., J.Org.Chem., 1970, 35(5), 1398–1404;
(vi) Lamberti et al., Recueil, 86 (1967) 504–510.

The 6-alkyl-alpha-pyrones of our invention, which are unsubstituted at the "4" position of the pyrone ring may also be prepared according to the process of Copending U.S. application for Letters Patent No. 471,756 filed on May 20, 1974 the reactions of which are as follows:

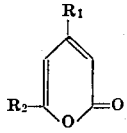


wherein R is alkyl.

THE INVENTION

It has now been discovered that tobacco flavoring compositions and tobacco products having sweet, aromatic, warm, spicy, maple-like, fruity, coumarin-like, vanillin-like, lactonic, lovage-like, celery-like and/or nut-like flavors and aromas prior to and on smoking may be provided by adding to tobacco flavors and/or

to tobaccos themselves one or more alpha pyrones having the generic structure:



wherein R_1 is hydrogen or methyl and R_2 is C_3–C_5 alkyl.

Thus, the groups exemplified by R_2 are as follows:

n-propyl
i-propyl
n-butyl
i-butyl
t-butyl
1-pentyl
2-pentyl
1-(2-methylbutyl)
2-(2-methylbutyl)
3-(2-methylbutyl)
1-(2,2-dimethylpropyl)

Specific examples of the compounds contemplated within the scope of our invention, and their tobacco flavor properties prior to and on smoking are as follows:

Compound	Organoleptic Properties Prior to Smoking	Organoleptic Properties On Smoking
6-n-propyl-alpha-pyrone	Creamy, sweet, coumarin, herbal note	Sweet, aromatic, lactone, coumarin, vanillin taste and aroma
6-n-butyl-alpha-pyrone	Sweet, slightly coumarin, and floral aroma	Sweet, aromatic, coconut, coumarin-vanillin, and lactone aroma and taste
6-i-butyl-alpha-pyrone	Sweet and coconut-like	Sweet, aromatic, and creamy-vanillin-like taste and aroma
6-n-pentyl-alpha-pyrone	Green, floral and coconut-like aroma	Fruity, coumarin-like taste and aroma
4-methyl-6-i-propyl-alpha-pyrone	Sweet, rum-like lovage, tagette with tonka undertone	Sweet, aromatic, warm spicy and lovage-like taste and aroma
4-methyl-6-n-butyl-alpha-pyrone	Sweet, coumarin-like, foenugreek like, celery-like aroma	Spicy, celery-like, fatty, creamy, cereal and nut-like taste and aroma
4-methyl-6-i-butyl-alpha-pyrone	Sweet, fruity, jasmine-like, appley aroma	Sweet, aromatic, warm, spicy, somewhat maple-like aroma and taste
4-methyl-6-n-pentyl-alpha-pyrone	Long lasting celery, lovage, tagette aroma	Maple, creamy, vanilla taste and aroma

It has been found that the tobacco additives of our invention when incorporated into tobacco products impart a flavor and aroma 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, as indicated in the above table, the compounds included within the broad scope of this invention may impart different flavors or aromas depending upon the alkyl 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.

In accordance with this invention, one or more of the alpha-pyrones of our invention, or mixtures thereof, is added to tobacco or applied to a smoking article or its component parts in amounts of about 100–5,000 parts per million (ppm) based on dry weight of the tobacco product. Preferably, the amount of additive is between about 200 and 500 ppm by weight in order to provide a tobacco product having a desired flavor and aroma. However, the amount used will depend upon the amound 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 percent ethyl alcohol solution of 6-n-pentyl-alpha-pyrone in an amount to provide a tobacco containing 200 ppm. 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 described as "fruity-coumarin-like" 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:

(a) Esters, for example:
Ethyl butyrate;
Ethyl acetate;
Ethyl valerate;
Amyl acetate;
Phenyl ethyl isovalerate; and
Methyl heptynyl carbonate

(b) Aldehydes, for example:
3-phenyl-2-pentenal;
3-phenyl-3-pentenal;
phenyl acetaldehyde;
Cinnamaldehyde; and
Beta-ethyl-cinnamaldehyde

(c) Ketones, for example:
Benzylidene acetone;
Acetophenone;

Maltol; and
Ethyl maltol
(d) Acetals, for example:
3-phenyl-4-pentenal dimethyl acetal; and
3-phenyl-4-pentenal diethyl acetal
(described in copending application for U.S. Letters Patent No. 276,922 filed on August 1, 1972)
(e) Natural oils and extracts, for example:
Vanilla;
Coffee extract;
Origanum Oil;
Cocoa Extract;
Oil of Cloves;
Nutmeg Oil;
Celery seed oil;
Bergamot oil; and
Ylang-ylang oil
(f) Lactones, for example:
Delta-decalactone;
Delta-undecalactone;
Delta-dodecalactone;
Gamma-undecalactone; and
Coumarin
(g) Ethers, for example:
Dibenzyl ether;
Vanillin; and
Eugenol
(h) Pyrazines, for example:
2-Acetyl pyrazine;
2-Acetyl-6-methyl pyrazine;
2-Ethyl pyrazine;
2,3-Dimethyl pyrazine;
2,5-Dimethyl pyrazine; and
2-Ethyl-5-methyl pyrazine
(i) Pyrroles, for example:
N-cyclopropyl pyrrole; and
N-cyclooctyl pyrrole

as well as those additives disclosed in United States Patent Nos. 2,766,145, 2,905,575, 2,905,576, 2,978,365, 3,041,211, 2,766,149, 2,766,150, 3,589,372, 3,288,146, 3,402,051 and 3,380,457 as well as Australian Patents 444,545, 444,507 and 444,389 may be incorporated into the tobacco with the additives 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.

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.

The following examples are given to illustrate the embodiments of the invention as it is presently preferred to practice it. It will be understood that these examples are illustrative and the invention is not to be considered as restricted thereto except as indicated in the appended claims.

EXAMPLE I

TOBACCO USE OF 6-ALKYL-ALPHA-PYRONE

The following tobacco flavor formulation (A) is prepared:

Ingredients	Parts
Ethyl Butyrate	0.05
Ethyl Valerate	0.05
Maltol	2.00
Cocoa Extract	26.00
Coffee Extract	10.00
Ethanol (95% aqueous)	20.00
Water	41.90

A tobacco formulation (B) is prepared as follows:

Ingredients	Parts
Bright Tobacco	40.1
Burley Tobacco	24.9
Maryland Tobacco	1.1
Turkish Tobacco	11.6
Stem (Flue-cured) Tobacco	14.2
Glycerine	2.8
Water	5.3

The flavor formulation (A) is added to a portion of the smoking tobacco formulation (B) at the rate of 0.1 percent by weight of the tobacco. The flavored and non-flavored tobacco formulations are then formulated into cigarettes by the usual manufacturing procedures:

(i) At the rate of 200 ppm to one-seventh of the cigarettes in each group is added 4-methyl-6-n-pentyl-alpha-pyrone. The use of the 4-methyl-6-n-pentyl-alpha-pyrone in the cigarettes causes the cigarettes prior to smoking to have a celery, lovage, tagette aroma. In smoke flavor, these notes are not found, however, on smoking the cigarettes containing the 4-methyl-6-n-pentyl-alpha-pyrone are found to be more richer, sweeter and spicier and to have maple, creamy and vanilla notes whether or not the other flavor ingredients of formulation (A) are present.

(ii) At the rate of 200 ppm to one-seventh of the cigarettes in each group is added 4-methyl-6-n-butyl-alpha-pyrone. The use of the 4-methyl-6-n-butyl-alpha-pyrone at this level causes the tobacco prior to smoking to have a sweet coumarin-like, foenugreek-like and celery-like aroma. On smoking, the foenugreek-like aroma is not perceived in the smoke flavor. However, the cigarettes are found to have a spicy, celery-like, fatty, creamy, cereal and nut-like aroma and taste and to be sweeter and spicier than the same formulation without the 4-methyl-6-n-butyl-alpha-pyrone whether or not the other flavor ingredients of formulation (A) are present therein.

(iii) At the rate of 500 ppm to one-seventh of the cigarettes in each group is added 6-n-propyl-alpha-pyrone. The use of the 6-n-propyl-alpha-pyrone in the cigarettes causes the cigarettes prior to smoking to have a creamy, sweet coumarin-like, herbal aroma. In smoke flavor, the herbal note is not found, however, on smoking, the cigarettes containing the 6-n-propyl-alpha-pyrone are found to have a sweet, aromatic, lactone, coumarin, vanillin-like taste and aroma, whether or not the other

flavor ingredients of formulation (A) are present.

(iv) At the rate of 200 ppm to one-seventh of the cigarettes in each group is added 4-methyl-6-isopropyl-alpha-pyrone. The use of the 4-methyl-6-isopropyl-alpha-pyrone at this level causes the tobacco prior to smoking to have a sweet rum-like, lovage, tagette aroma with a "tonka" undertone. On smoking, rum-like aroma is not perceived in the smoke flavor. However, the cigarettes are found to have sweet, aromatic, warm, spicy, lovage-like taste and aroma notes not existing in the same formulation without the 4-methyl-6-isopropyl-alpha-pyrone whether or not the other flavor ingredients of formulation (A) are present therein.

(v) At the rate of 500 ppm to one-seventh of the cigarettes in each group is added 6-n-butyl-alpha-pyrone. The use of the 6-n-butyl-alpha-pyrone at this level causes the tobacco prior to smoking to have a sweet and floral aroma with a slight coumarin-like character. On smoking, the floral note is not perceived in the smoke flavor. However, the cigarettes on smoking are found to have a sweet, aromatic, coconut, coumarin-vanillin, lactone taste and aroma, whether or not the other flavor ingredients of formulation (A) are present.

(vi) At the rate of 200 ppm to one-seventh of the cigarettes in each group is added 6-n-pentyl-alpha-pyrone. The use of 6-n-pentyl-alpha-pyrone at this level in the cigarettes causes the cigarettes prior to smoking to have a green, floral and coconut aroma, significantly more intense than cigarettes containing delta-dodecalactone. In smoke flavor, these notes are not found, however, on smoking, the cigarettes containing the 6-n-pentyl-alpha-pyrone are found to have a marked fruity, coumarin-like taste and aroma whether or not the other ingredients in formulation (A) are present.

One-seventh of the cigarettes remains totally without added flavorants. One-seventh of the cigarettes contains only formulation (A) added thereto; but no 6-alkyl-alpha-pyrone.

In general, on smoking, the cigarettes containing the exemplified 6-alkyl-alpha pyrones are more coumarin-like and/or sweeter, warmer, spicier and more aromatic in nature than those cigarettes not containing these 6-alkyl-alpha pyrones whether or not ingredients of formulation (A) are included in the tobacco.

It will be understood by those skilled in the art from the foregoing description that the 6-alkyl-alpha-pyrones of our invention can be used in the preparation of a wide variety of tobacco flavors and products.

EXAMPLE II

TOBACCO FLAVOR FORMULATION CONTAINING 6-ALKYL-ALPHA-PYRONES

A tobacco flavor formulation is prepared by admixing the following ingredients:

Ingredients	Parts
6-n-pentyl-alpha-pyrone	2.0
Ethyl Butyrate	0.5
Ethyl Valerate	0.5
Maltol	20.0
Cocoa Extract	260.0
Coffee Extract	100.0
95% Aqueous Ethanol	200.0
Water	419.0

This formulation is added to smoking tobacco at the rates of 0.01, 0.02, 0.03 and 0.035 percent based on the dry weight of the tobacco. The tobacco is then manufactured into cigarettes according to standard manufacturing practice. On smoking the cigarettes, the aroma and taste is described as "fruity, coumarin-like" with intensity of the "fruity-coumarin" quality, increasing with increasing concentration of the flavor formulation in the tobacco.

EXAMPLE III

TOBACCO FLAVOR FORMULATION

A tobacco flavoring formulation is prepared by admixing the following ingredients:

Ingredients	Parts
Cinnamaldehyde	30.60
Nutmeg Oil, EI	0.50
Dibenzyl Ether	3.70
Eugenol	1.20
4-methyl-6-n-butyl-alpha-pyrone	3.00
Vanillin	0.50
3-Phenyl-4-pentenal dimethyl acetal prepared according to the process disclosed in copending application for U.S. Letters patent 276,922 filed on August 1, 1972	60.00

The foregoing formulation is added to smoking tobacco at the rate of 0.06–0.15 percent based on the dry weight of tobacco. The purpose of the use of the 3-phenyl-4-pentenal dimethyl acetal is to provide to the flavor on smoking a cinnamon powder aroma and taste. The 4-methyl-6-n-butyl-alpha-pyrone (concentration on tobacco: 1800–4500 ppm) acts as an excellent replacement for the coumarin, formerly used in this formulation, and also enables the previously-used quantity of vanillin to be halved.

A formulation yielding substantially the same results is produced when one-half of the 4-methyl-6-n-butyl-alpha-pyrone used is replaced with an equal quantity (1.50 parts by weight) of 4-methyl-6-n-pentyl pyrone.

EXAMPLE IV

TOBACCO FLAVOR FORMULATION

A tobacco flavoring formulation is prepared by admixing the following ingredients:

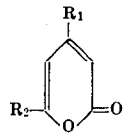
Ingredients	Parts
Bergamot Oil, Italy	5.00
Ylang-ylang oil	1.20
4-methyl-6-n-pentyl-alpha-pyrone	1.20
Acetophenone	1.20
Phenyl acetaldehyde	0.50
Phenyl ethyl isovalerate	1.00
Methyl heptynyl carbonate	0.50
3-Phenyl-4-pentenal diethyl acetal prepared according to the process disclosed in copending application for U.S. Letters Patent 276,922 filed on August 1, 1972	20.00
95% Aqueous Ethanol	69.40

The foregoing flavor is added to smoking tobacco at the rates of 0.10, 0.20 and 0.30 percent based on the weight of dry tobacco. The tobacco is then manufactured into cigarettes according to standard manufacturing practice. The purpose of the 3-phenyl-4-pentenal diethyl acetal is to cause the tobacco, on smoking, to

have a hay-clover-like flavor with fruity notes. The 4-methyl-6-n-pentyl-alpha-pyrone (at concentrations, based on the dry weight of tobacco, of 1,200–3,600 ppm) acts as an excellent replacement for the coumarin, previously used in this formulation.

We claim:

1. A tobacco product comprising tobacco, said product having added thereto a small amount sufficient to alter the flavor or aroma of the tobacco product of one or more 6-alkyl-alpha-pyrone compound having the formula:



wherein R_1 is selected from the group consisting of methyl and hydrogen; and R_2 is C_3–C_5 alkyl.

2. The tobacco product of claim **1** wherein the 6-alkyl-alpha-pyrone compound is selected from the group consisting of:

(i) 6-n-propyl-alpha-pyrone;
(ii) 6-n-butyl-alpha-pyrone;
(iii) 6-n-pentyl-alpha-pyrone;
(iv) 4-methyl-6-isopropyl-alpha-pyrone;
(v) 4-methyl-6-n-butyl-alpha-pyrone;
(vi) 4-methyl-6-isobutyl-alpha pyrone; and
(vii) 4-methyl-6-n-pentyl-alpha-pyrone,

and mixtures thereof.

3. The tobacco product of claim **1** wherein the concentration of 6-alkyl-alpha-pyrone in the tobacco product is from 100–5000 parts per million, based on the total weight of tobacco on a dry basis.

4. The tobacco product of claim **1** wherein the concentration of 6-alkyl-alpha-pyrone in the tobacco product is from 200–500 parts per million, based on the total weight of tobacco on a dry basis.

5. The tobacco product of claim **2** wherein the concentration of 6-alkyl-alpha-pyrone in the tobacco product is from 200–500 parts per million based on the total weight of tobacco product on a dry basis.

6. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 6-n-propyl-alpha-pyrone.

7. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 6-n-butyl-alpha-pyrone.

8. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 6-n-pentyl-alpha-pyrone.

9. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 4-methyl-6-isopropyl-alpha-pyrone.

10. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 4-methyl-6-n-butyl-alpha-pyrone.

11. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 4-methyl-6-isobutyl-alpha-pyrone.

12. The tobacco product of claim **4** wherein the 6-alkyl-alpha-pyrone is 4-methyl-6-n-pentyl-alpha-pyrone.

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