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TOBACCO PRODUCT

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12 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.

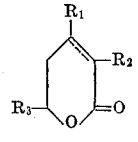
A further object of this invention is the provision of a process for enhancing or otherwise improving the flavor, aroma and other qualities of certain domestic, oriental, reconstituted or synthetic tobaccos which may be deficient in said flavor or aroma or other qualities.

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 which has been treated with a small amount of a compound selected from the group of compounds having the formula



Formula I

wherein R_1, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups, with at least one of such substituents being alkyl. Thus, the tobacco additives of the present invention are alkyl substituted, saturated or unsaturated δ lactones. Preferably the alkyl radicals present in the tobacco additives are lower alkyl radicals of 1 to 6 carbon atoms. Thus, the alkyl substituents can be, for example, methyl, ethyl, propyl, isopropyl, normal butyl, isobutyl, pentyl or hexyl.

The following specific examples illustrate the preparation and characteristics of representative tobacco additives of the present invention. It will be appreciated, however, that this invention is not limited to the specific process

by which the compounds may be prepared. All temperatures are expressed in degrees centigrade.

Example I.—Synthesis of 3-isopropyl-δ-valerolactone

(a) *3-isopropyl glutaric acid.*—To a vigorously stirred solution of 94 grams of α-cyanoacetamide in 700 milliliters of water at 15° C. were added 35 grams of isobutyraldehyde and 10 grams of piperidine. Stirring was continued for 3 hours while the reaction mixture was kept between 10–15° C. The reaction mixture was then placed in the freezer overnight (16 hours). After allowing the solidly frozen reaction mixture to thaw the fine, white crystals were collected on a Buchner funnel, washed and dried to yield 81.8 grams (82% of theory), of the α,α-dicyano-β-isopropyl glutaramide (M.P. 152–154°). Without further purification 80 grams of this product was placed in a 1 liter round bottom flask equipped with a reflux condenser; 300 milliliters of concentrated hydrochloric acid was added and the solution was brought to gentle reflux temperature. After 6 hours refluxing another 25 milliliters of hydrochloric acid was added and refluxing continued (another check after 12 hours indicated the hydrochloric acid content was still high) for a total of 29 hours. This hot solution was then poured into an evaporating dish, where upon cooling a volume of light tan solids precipitated out of solution. The solids were filtered from the solution in a Buchner funnel and thoroughly washed with methylene chloride (they were mostly soluble in this organic solvent). Extraction of the aqueous extraction solution with methylene chloride furnished 19 grams of the β-isopropyl glutaric acid, melting point 98–101°. A further extraction of the aqueous reaction solution with methyl ethyl ketone provided another 33 grams of the title compound; total 52 grams, 83% of theory. A 1 gram sample of the crude isopropyl glutaric acid was recrystallized from 10% hydrochloric acid to raise its melting point to 103–104° [lit. 102°].

(b) *3-isopropyl-glutaric anhydride.*—A 500 milliliter round bottom flask was equipped with reflux condenser and heating mantle. The flask was charged with 49 grams of the crude 3-isopropyl gluartic acid and 50 milliliters of acetic anhydride and brought to reflux temperature for 6 hours. The refluxed solution was then transferred to a 250-milliliter flask equipped with a 15 centimeter Vigreaux column distilling head. After distilling off the acetic acid at atmospheric pressure the system was brought under reduced pressure. After removal of the remaining acetic anhydride 44.3 grams of the title compound were collected; boiling point 122–126°/750μ. A previous 2 gram fraction, collected at boiling point 117°/750μ, was also the 3-isopropyl glutaric anhydride; total 46.3 grams, 98% yield.

(c) *Ethyl hydrogen-3-isopropyl glutarate.*—This compound was prepared in the usual manner by alcoholysis of the anhydride. A 200 milliliter round bottom flask was equipped with reflux condenser, drying tube, and charged with 44.3 grams (0.284 mole) of the anhydride and 13.08 grams (0.284 mole) of anhydrous ethanol and brought to full reflux on the steam bath for one hour and allowed to stand overnight (15 hours). An infrared spectrum of this faintly colored solution indicated that the half-ester was present in high percentage. This reaction mixture was distilled under vacuum and 3 fractions were collected after a forerun of 1 milliliter of ethanol was distilled off. The tabulated data are below:

TABLE I.—DISTILLATION OF ETHYLHYDROGEN-3-ISOPROPYL GLUTARATE

Fraction	Vapor Temp. (deg.)	Pressure (μ)	Product
1	70–80	350	Diester (ca. 1 ml.) (IR).
2	80–115	350	2.3 g. monoester +trace of diester.
3	125–126	300	47.61 g. monoester (IR & NMR).

1 gram of yellow pot residue was discarded; 87% yield of the title compound.

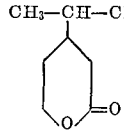
(d) *dl-3-isopropyl-δ-valerolactone.*—A 3-neck, 1 liter flask was set up on the steam bath and equipped with reflux condenser, drying tube and mechanical stirrer (all equipment thoroughly dried). The flask was charged with 300 milliliters of tetrahydrofuran that had been freshly distilled from calcium hydride and 45.7 grams (0.226 mole) of ethylhydrogen-3-isopropyl glutarate. To this vigorously stirred solution was added 24.4 grams (0.45 mole) of potassium borohydride followed by 11 grams of lithium chloride. This mixture was stirred at room temperature for 0.5 hour before turning the steam into the bath. Upon heating a vigorous reaction with evolution of gas set in; the stirred mixture was kept at a gentle reflux for 4.5 hours. After cooling to room temperature the reaction was hydrolyzed in the usual manner with dilute hydrochloric acid and thoroughly extracted with ether. After drying the ether solution the ether was removed by distillation over a steam bath and the residue was transferred to a 100 milliliter distilling flask equipped with 15 centimeter Vigreaux column and fraction collecter for distillation under reduced pressure. The results are tabulated below:

TABLE II.—DISTILLATION OF 3-ISOPROPYL-δ-VALEROLACTONE

Fraction	Vapor Temp. (deg.)	Pressure (μ)	Weight (g.)	Product
1	85–89	800	18.4	3-isopropyl-δ-valerolactone (IR).
2	90–105	800	2.28	Lactone+diol.
3	106	750	2.55	3-isopropyl-1,5-pentanediol (IR).

[1] A 7 gram residue of very viscous material was left in the distilling flask. It proved to be the diol contaminated with boric acid.

The tobacco additive dl-3-isopropyl-δ-valerolactone has the following structure:

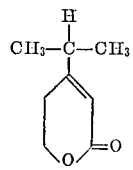


It is a water-white liquid, boiling point 59°/90μ, 139°/14 millimeters; infrared spectrum: 5.8 (vs), 7.95 (s), 8.2 (s) and 9.25 (vs) μ; nuclear magnetic resonance spectrum:

τ=9.08(6) (split, isopropyl), 7.62 [(2)—CH_2—CO—] and 5.77 [(2)—CH_2O—]; $C_8H_{14}O_2$, mass=142.

Example II.—5-hydroxy-3-isopropyl-2-pentenoic acid, δ-lactone

To a solution of 1 gram of β-isopropyl-δ-valerolactone prepared according to the method of Example I, in 10 milliliters of carbon tetrachloride were added 1.8 grams of N-bromosuccinimide; and the mixture was refluxed 1.5 hours under irradiation with an infrared heat lamp. Filtration of the solution followed by concentration gave a residue which was heated in an oil bath with 5 milliliters of dimethylaniline at 60° for one hour. The solution was diluted with 25 milliliters of water, extracted with ether, and the ether layer was washed with 100 milliliters of 5 N hydrochloric acid and concentrated. Vapor phase chromatography of the residue gave mainly one substance which was shown by infrared and nuclear magnetic resonance spectroscopy to have the formula:

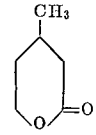


Example III.—5-hydroxy-2-isopropylhexanoic acid, δ-lactone

To a solution of 16.3 grams of 5-keto-2-isopropylhexanoic acid, prepared by the method of Bardhan, De, and Dalta, J. Chem. Soc., 3195 (1951), in 50 milliliters of 95% ethanol was added 15 grams of potassium borohydride in small portions until the reaction ceased. The solution was refluxed for one hour, cooled, acidified with 10% sulfuric acid and extracted with ether. Concentration of the ether layer gave 5-hydroxy-2-isopropylhexanoic acid as an almost colorless oil. This hydroxy acid was heated on an oil bath at 180° for one hour and distilled under reduced pressure; 7.2 grams of 5-hydroxy-2-isopropylhexanoic acid, δ-lactone, boiling point 112–115°/8 millimeters, were obtained. The lactone was identified from its infrared and nuclear magnetic resonance spectra.

Example IV

β-Methyl-δ-valerolactone is a commercially available chemiral having the formula



It is a water-white liquid, boiling point 100°/10 millimeters; infrared spertrum: 5:77 (vs), 7.95 (s), 8.15 (s), 9.20 (s); nuclear magnetic resonance spectrum: τ=8.92 and 9.0 [(3) methyl], 7.50 and 7.37 [(2)—CH_2—CO—] and 5.74 [(2)—CH_2O—]; $C_6H_{10}O_2$, mass=114.

It has been found that the tobacco additives of the 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, 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. The tobacco additive of Example I imparts an aroma and flavor which is reminiscent of coconut which many smokers consider to be desirable in a tobacco product. The tobacco additive of Example II imparts an aroma and flavor which some characterize as coconut; the tobacco additive of Example III has a spicy note; and that of Example IV has a spicy apple note.

In accordance with this invention, a compound embraced by generic formula I, or mixtures thereof, is added to tobacco or applied to a smoking article or its component parts in amounts of about 0.01 to 2.0 percent by weight of the product. Preferably the amount of additive is between about 0.1 and 0.5 percent by weight in order to provide a tobacco product having a desired flavor and aroma. 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 to-

bacco 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 3-isopropyl-δ-valerolactone in an amount to provide a tobacco containing 0.2 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 coconut 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.

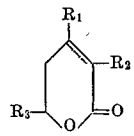
While this invention is principally useful in the manufacture of cigarette tobacco, it is also suitable for use in connection with the manufacture of pipe tobacco, cigars or other tobacco products. Furthermore, the compounds may be added to certain tobacco substitutes of natural or synthetic origin and 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 modifications as fall within the true spirit and scope of this invention.

We claim:

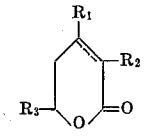
1. A tobacco product having added thereto an amount sufficient to alter the flavor or aroma of the tobacco product of a compound selected from the group of compounds having the formula



Formula I

wherein R_1, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups with at least one of such substituents being alkyl.

2. 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 of compounds having the formula



Formula

wherein R_1, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups of 1 to 6 carbon atoms, with at least one of such substituents being alkyl.

3. The product recited in claim **1** wherein the amount of said compound is between about 0.01 and 2.0 percent by weight of the product.

4. The product recited in claim **1** wherein the amount of said compound is between about 0.1 and 0.5 percent by weight of the product.

5. A tobacco product having added thereto and dispersed therein a small amount sufficient to improve the flavor thereof of 3-isopropyl-δ-valerolactone.

6. A tobacco product having added thereto and dispersed therein a small amount sufficient to improve the flavor thereof of 5-hydroxy-3-isopropyl-2-pentenoic acid-δ-lactone.

7. A tobacco product having added thereto and dispersed therein a small amount sufficient to improve the flavor thereof of β-methyl-δ-valerolactone.

8. A tobacco product having added thereto and dispersed therein a small amount sufficient to improve the flavor thereof of 5-hydroxy-2-isopropylhexanoic acid.

9. The product recited in claim **5** wherein the amount of flavorant is between about 0.01 and 2.0 percent by weight of said product.

10. The product recited in claim **6** wherein the amount of flavorant is between about 0.01 and 2.0 percent by weight of said product.

11. The product recited in claim **7** wherein the amount of flavorant is between about 0.01 and 2.0 percent by weight of said product.

12. The product recited in claim **8** wherein the amount of flavorant is between about 0.01 and 2.0 percent by weight of said product.

References Cited

UNITED STATES PATENTS

2,766,149	10/1956	Rowland	131—17
2,766,150	10/1956	Teague	131—17

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D. J. DONOHUE, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,380,457 April 30, 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:

Columns 3 and 4, TABLE II, fourth column, line 3, "2.55" should read -- ^{1}2.55 --. Column 4, line 16, "chemiral" should read -- chemical --; line 32, "spertrum: 5:77" should read -- spectrum: 5.77 --. Column 6, line 14, "Formula" should read -- Formula I --.

Signed and sealed this 7th day of October 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents