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LACTIC ACID ESTERS OF POLYISOPRENOID ALCOHOLS

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This invention has to do with a tobacco or tobacco-like product having improved smoking characteristics. More particularly, it relates to enhancing the flavor of tobacco-containing products, to novel tobacco products, to certain novel compositions for use with tobacco, and to processes for preparing such compositions and products.

The term "tobacco" as used in this specification and the appended claims means and includes, where the context permits, natural tobaccos such as burley, Turkish tobacco, Maryland tobacco, Virginia tobacco, and flue-cured tobacco; tobacco-like products such as reconstituted tobacco or homogenized tobacco; and tobacco substitutes intended to replace natural tobacco such as various vegetable leaves, for example lettuce and cabbage leaves and the like.

There has been a marked trend in the tobacco industry toward the use of filters in cigarettes, cigars and pipes. In addition, applications have been found for reconstituted or homogenized tobaccos and for synthetic wrappers and fillers as substitutes for natural tobacco. Such smoking products have suffered from poor flavor characteristics. They are generally regarded as harsh, as containing undesirable aroma quality, and otherwise are considered as having poorer smoking flavor and less pleasant smoking character. These innovations have accentuated the need for improving the flavor of tobacco products and otherwise enhancing the smoking characteristics of these products. Oftentimes improved flavor may be obtained by the use of higher grade tobacco leaf. However, this is costly, the supply of certain types of leaf has been limited, and there has accordingly been increased use of tobacco stems and poorer grades of tobacco in various blends.

It has been suggested that various additives or flavoring agents be incorporated with, or added to, tobacco products to improve their flavor. These additives and agents have not been uniformly successful because they have suffered from a number of disadvantages. The main disadvantages of the additives and agents previously proposed for this purpose have been their relative unavailability, high cost, and inferior aroma and flavor.

Accordingly, this invention provides an improvement in the flavor and smoking characteristics of tobacco products.

Further and more specific objects, features, and advantages will clearly appear from the detailed description given below.

The invention comprises the novel products as well as the novel processes and steps of processes according to which such products are manufactured, the specific embodiments of which are described hereinafter by way of example and in accordance with which it is now preferred to practice the invention.

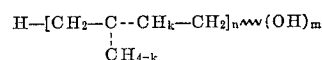
In accordance with this invention it has been found that tobacco materials can be improved in flavor and smoking characteristics by incorporating in, or adding to, such materials a small but effective amount of one or more novel lactic acid esters of a polyisoprenoid alcohol or alcohols. Such esters of polyisoprenoid alcohols are produced by novel processes. Tobacco or tobacco-like products containing a lactic acid ester of a polyisoprenoid

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alcohol, or mixtures of such esters are milder and less harsh and have a pronounced tobacco taste and character. This improved taste, character and flavor is noted even when the tobacco is smoked through a filter.

The lactic acid esters of polyisoprenoid alcohols of this invention have been found to possess a combination of properties which makes them particularly suitable as tobacco flavoring agents in that such compositions are effective at low concentrations and thus will not bleed into tobacco wrapping materials, are low in cost, are stable on prolonged storage, are not known to decompose on smoking to give materials which are physiologically harmful, and their flavor enhancement is effective even through a filter. The use of the lactic acid esters of polyisoprenoid alcohols of this invention as tobacco flavoring agents also permits greater flexibility in utilizing new blends of tobacco.

The tobacco flavoring agents of this invention are lactic acid esters of polyisoprenoid alcohols and such alcohols are represented by the following formula:



wherein n is an integer of 4 or more; the dotted lines mean that the bond at the positions indicated is either a single or a double bond, one double bond being present in each isoprene unit, except those containing a tertiary hydroxyl; and k is 1 or 2, the value of k being determined by the position of the double bond. The alcohol molecule contains at least one hydroxyl and can contain several hydroxyls, so that m is at least one. The wavy line indicates that the hydroxyl(s) can be terminal or substituent on the chain. It will be understood that in molecules containing no primary allylic hydroxyl the terminal group will be a conjugated dienolic system or a cyclic, e.g., menthenyl, system. The IR, UV, and nuclear magnetic resonance data show the presence of vinylidene methylene groups, tri-substituted double bonds, primary allylic hydroxyls, and tertiary hydroxyls, and are suggestive of groups such as terminal menthenyls.

The formula given as representative of the polyisoprenoid alcohols contemplates and includes all of the foregoing variations and mixtures thereof. Exemplary polyisoprenoid alcohols include

- 2,6,10,14-tetramethyl-2,6,10,14-hexadecatetraene-16-ol;
- 16-(1-methyl-4-isopropenyl-cyclohexyl)-2,6,10,14-tetramethyl-2,10,14-hexadecatriene-6-ol;
- 2,6,10,14,18,22,26-heptamethyl-2,6,10,14,18,22,26-octacosaeptaene-28-ol;
- 2,10,18,26-tetramethyl-6,14,22-trimethylene-2,25,27-octocosatriene-10,18-diol;
- 2,6,10,14,18,22,26,30,34-nonamethyl-2,6,10,14,18,22,26,30,34-hexatriacontanonaen-36-ol;
- 2,6,10,14,18,22,26,30,34,38,42,46-octatetracontadecaen-48-ol; and
- 2,6,10,14-tetramethyl-1,10,14-hexadecatriene-6,16-diol.

It should be understood that the polyisoprenoid alcohol precursors represented by the above formula can include additional hydroxy groups in the chain or can have other tertiary hydroxy groups, and such materials are considered equivalent for purposes of this invention.

It is desirable that n in the foregoing formula be at least four, because at lower values the esters may have odors of their own, and such odors can detract from the taste of the tobacco when it is smoked. It is preferred that the ester be odorless so that the character of the tobacco before smoking will not be adversely affected. Very high molecular weight isoprenoid alcohols can be used in producing the esters of this invention, but for ease of han-

dling and processing, it is desirable that very high molecular weight materials be excluded, and it is accordingly preferred that n in the above formula be an integer from about 4 to about 15, inclusive. The infrared absorption of the alcohols at 8.6–8.9 and at 10.0 microns indicates the presence of tertiary hydroxyl and primary allylic hydroxyls, respectively; and the UV absorption at 240 millimicrons, conjugated dienes.

To produce the lactate esters the foregoing alcohols are esterified with lactic acid, the acid desirably being present in quantities at least equimolar with the isoprenoid alcohols. For the majority of uses, it is preferred that the lactic acid be esterified with the isoprenoid alcohol or alcohols in a proportion of from about 3 to about 25 molecules of lactic acid for each molecule of isoprenoid alcohol. It is believed that the polyisoprenoid lactate esters of this invention are, at least in some instances poly-lactates, that is, that the carboxylic acid group of a lactic acid molecule forms an ester with the hydroxyl group of a lactic acid molecule which is esterified with an isoprenoid hydroxy group. The free lactic hydroxyl group may in turn be esterified with another lactic carboxylic group, and so on. Molecular ratios of lactic acid to isoprenoid alcohol in the range of from about 6 to about 18 give superior taste improvement in tobacco, and ratios of about 9 are greatly preferred because such ratio is optimum for many tobaccos.

The lactate esters of this invention can have acid contents of from nil to about 0.045, alcohol contents from about 0.4 to about 2.5, and ester contents of from about 0.3 to about 7.5. All acid, alcohol, and ester contents are expressed herein in milliequivalents of reagent per gram of sample, as determined by standard analytical methods. While certain IR ranges in the lactates are obscured, the 240 millimicron UV absorption indicates 0.2–0.3 mole dienoic material per mole of lactate (based on a molecular weight of 550–600 for the alcohol).

Briefly, the process of this invention for the preparation of lactate esters involves the reaction of isoprene and carboxylic acid to form polyisoprenoid alcohol carboxylic acid esters and the esterification of the carboxylate so formed with a suitable lactic acid material to form the polyisoprenoid alcohol lactate. Generally it is necessary to purify the material during at least one step of the process so as to obtain the desired chain length in the isoprenoid material. Moreover, it is frequently helpful to separate the lactic esters into different fractions depending upon their ultimate use, as further disclosed hereinafter.

A wide variety of steps and sequences of steps can be used in practicing the process. The isoprene is polymerized at low pH in the presence of a carboxylic acid. The carboxylate polymer so formed can then be separated into the desired fractions before reaction to form the lactate or the polymer can be reacted directly with a lactate material to form the esters by transesterification. If the fractions are separated, the desired fraction can be saponified to produce the free alcohol and then reacted with lactic acid or a lactate to produce the polyisoprenoid alcohol lactate of this invention. Alternatively, the entire mass of polymerized isoprene can be saponified to form the alcohol and the alcohol can be purified and reacted with a lactic acid or lactate to form the polyisoprenoid alcohol lactate or the alcohol can be reacted with the lactic acid or lactate to form esters and then the esters purified or separated as desired. Certain desirable processes for the practice of this invention are disclosed below and embodiments thereof described in the examples.

The first step in the process when isoprene is the starting material is the preparation of a polyisoprenoid material. The polyisoprenoid alcohol precursors from which the lactic acid ester flavoring agents of this invention are derived are preferably obtained from the controlled polymerization of isoprene in a lower aliphatic carboxylic acid. In general, the controlled polymerization of isoprene is of the ionic type, and is preferably carried out by

reacting isoprene in a lower aliphatic carboxylic acid and in the presence of a strong acid catalyst, preferably at a pH of 3 or less, under controlled temperatures for a period sufficient to obtain the desired number of isoprene units in the polymer. Any lower aliphatic carboxylic acid can be used, although saturated lower alkyl monocarboxylic acids such as acetic acid, propionic acid, and the like are preferred. The strong acid catalyst can be a mineral acid such as sulfuric acid and phosphoric acid, or acidic resins such as sulfonated polystyrene resins like Amberlyst 15 made and sold by Rohm & Haas Company, and other strong acid equivalents.

The temperature and duration of the reaction will depend on a variety of factors including the economics of reaction time and conversions desired and the specific organic acid and catalyst employed. At low temperatures the reaction time becomes excessive, while at temperatures much above 70° C. the reaction may proceed too quickly, higher polymers of isoprene may be formed, and a closed system and superatmospheric pressure is required to prevent loss of the volatile isoprene. Generally, the reaction temperature can vary from about 15° C. to 70° C., and temperatures of from about 25° C. to 35° C. are preferred. Depending upon the temperature chosen, the time of the reaction can vary from about 5 to 200 hours, and preferably the reaction period is from about 50 to about 170 hours.

When the reaction is completed, the acid catalyst is neutralized by the addition of a basic material or removed from the reaction mixture, and the unreacted materials and the reaction products containing less than four isoprene units per molecule can be separated by any conventional method. Preferably, such products are separated by distillation, and vacuum distillation is desirable. The residue from this separation containing products of four and more isoprene units per molecule can further be refined by high vacuum distillation, and short path, thin film, or molecular, distillation is preferred. The distillate from the molecular distillation contains polyisoprenoid lower alkyl carboxylates which are then used to produce the polyisoprenoid alcohols used as precursors in this invention or are transesterified with a desired lactate material.

Preparation of the lactic acid esters of polyisoprenoid alcohols in accordance with this invention can be accomplished by any of the conventional techniques including transesterification with an alkyl lactate, preferably a lower alkyl lactate, at elevated temperatures in the presence of a solvent, preferably a hydrocarbon solvent, and a basic material such as an alkali-metal alcoholate; saponification of the polyisoprenoid ester to the alcohol followed by direct esterification of lactic acid with the polyisoprenoid alcohols at elevated temperature in the presence of a dehydrating agent such as concentrated sulfuric acid; or trans- or cross-esterification of the alcohol with a lower alkyl lactate, e.g., ethyl lactate or butyl lactate with the polyisoprenoid alcohol in an inert solvent such as an aromatic hydrocarbon, for example, benzene, toluene or the like, and in the presence of a basic material such as an alkali-metal alcoholate or the like.

The temperature of the reaction will depend upon the type of esterification procedure and the pressure used. The pressure can be atmospheric or sub- or superatmospheric. When normal atmospheric pressures are used, the preferred temperature for the esterification ranges from about 70° C. to about 125° C. The esters can be purified by simple distillation of the volatiles, and the ester recovered from the residue by distillation, preferably short path, thin film, high vacuum distillation. Preparation of the lactic acid esters of polyisoprenoid alcohols by transesterification is preferred for in this way undesirable side reactions are minimized. For example, by the transesterification method of preparing the esters, polymerization of lactic acid can be controlled and dehydration of the polyisoprenoid alcohols is minimized.

The particular polyisoprenoid lactic acid ester or esters of this invention are selected according to the type of smoking and sidestream character desired, the type of tobacco being utilized, the type of product to be improved (e.g., regular or filter cigarettes, cigars, or pipe tobacco), the processing method and conditions, and the particular character of product desired. The term "sidestream" as used herein means the smoke resulting directly from burning the tobacco in distinction from the flavor and aroma obtained by drawing smoke through the tobacco.

As is known, different tobaccos have different characteristics depending on the type of tobacco, the variety of tobacco, the type of soil on which it is grown, the types and amounts of fertilizer and micronutrients used, the weather conditions during the growing season, the part of the leaf or plant which is incorporated, and subsequent treatment of the leaf after it is severed from the plant. For illustration, some tobaccos have foreign flavors and aromas such as earthy, acrid, or paper-like when they are smoked. Illustrative of tobaccos with such foreign notes are black tobaccos; stems; reconstituted tobacco sheet; Argentine, Mexican, and other tobaccos produced in South and Central America, Africa, and Asia; and the like. On the other hand some low-grade tobaccos have little or no flavor at all. These low-grade tobaccos are relatively flavorless due to the growing conditions, the variety of plant, the stalk position of the leaf, or certain curing operations. Still other tobaccos are harsh and have a strong impact in the throat. Generally these harsh tobaccos are those with a high alkaloid or high total volatile base content such as is formed in some burleys and in tobaccos grown in soil containing large quantities of available nitrogen.

The lactates produced according to this invention can, as described above, be separated into different fractions, as for example by distillation, or the entire range of lactates produced can be utilized. For example, the lactates can be separated into a large number of fractions which can be used singly or in combination to provide the desired smoking and sidestream characteristics in the tobacco. With many tobaccos, the smoking and sidestream characteristics can be improved by utilizing a range of lactates.

It has been found that the lower boiling lactates are particularly useful in improving the organoleptic characteristics of foreign-flavored tobaccos. The higher boiling lactates are particularly useful in improving low-grade or harsh tobaccos. Accordingly, while the entire range of lactates formed can be used to improve the flavor and aroma characteristics of tobaccos, especially the foreign-flavored tobaccos, in many instances it is preferred to separate the lactates into low- and high-boiling sections and to utilize the low boilers on foreign-flavored tobaccos and the high boilers on low-grade or harsh tobaccos. When a spinning disc molecular still having a rotor diameter of about five inches (such as the CMS-5 centrifugal molecular still made by Consolidated Vacuum Corporation, Rochester, N.Y.) is used at a pass rate of 20-25 gm./min., it is preferred to use the lactates obtained at rotor temperatures below about 85° for foreign-flavored tobaccos and the lactates obtained at rotor temperatures above about 75° C. for low-grade tobaccos.

The lactates of this invention can be applied directly to the tobacco or otherwise incorporated into the finished product. As examples, the lactates can be used to treat the paper wrappers for cigarettes or the tobacco leaf wrapper for cigars. It is desirable to add the lactates directly to the tobacco itself. The lactates can be added directly to the tobaccos as-is and they are preferably added with a vehicle in the form of solutions, suspensions, emulsions, and the like since the preferred usage levels are relatively low and the amount added is more easily controlled and evenly distributed when vehicles are used. For example, the lactates of this invention can be added by spraying the leaf with a solution, preferably an alco-

holic solution, of the lactate; such lactates can be added directly to the slurry from which reconstituted tobacco leaf is prepared; they can be added to tobacco stems and the like by spraying; they can be incorporated into the "casing" (the aqueous mixture of additives applied to blended leaf prior to cutting); they can be incorporated in "top flavors" (the materials added to the cut leaf after drying); and the like.

The lactic acid ester flavoring agent can be incorporated with the tobacco before or after blending a number of tobacco varieties, or the flavoring agent can be added to one or more of such tobacco varieties prior to blending. The agent can be added prior to or after aging the tobacco. The amount of the tobacco flavoring agent composition used depends upon a number of factors including the particular flavor or smoking character desired, the particular tobaccos used, the type of product, and the specific flavor agent composition employed.

Generally the flavoring agent mixture of this invention is admixed with tobacco or tobacco-like materials in amounts of from about 0.05 to 5.0 percent by weight based on the weight of the tobacco materials at their finished moisture content. At proportions below about 0.05 percent little improvement is detected and at proportions much above about 2.0 percent non-tobacco characteristics or objectionable flavors or aromas may be produced. Where low-grade tobaccos are treated with the flavoring agents of this invention, up to 5 percent of the agent can be present in this tobacco. These high levels are used chiefly in heavily-cased pipe tobaccos. The preferred usage level is from about 0.20 to about 1.0 percent. Where foreign-flavored tobaccos are treated, from about 0.50 to about 2.0 percent of the agent of this invention is preferred.

The tobacco flavoring agent compositions of this invention can also be combined with other flavor or aroma enhancing materials to obtain various pleasing combinations of qualities. These can be formulated as desired to obtain the particular flavor and aroma nuances required. Other smoke enhancing ingredients with which the compositions of this invention can be combined include essential oils, balsam, fruit flavors such as peach, walnut, and cherry, coriander, coumarin, lactic acid, and phenylacetic acid. Other nuances such as spice, nut fruit, rum, honey, and the like can be added to the compositions of this invention or used in conjunction therewith.

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

EXAMPLE I.—Preparation of polyisoprenoid acetate

To a flask fitted with reflux condenser, stirrer and thermometer 3000 gm. of isoprene, 3000 gm. of glacial acetic acid, 15 gm. of water, 7 gm. of hydroquinone and 10 gm. of concentrated sulfuric acid are charged. The mixture is stirred for six hours and then allowed to stand at about 25° C. for 120 hours with stirring for 30 minutes after each 24-hour period.

The catalyst is then neutralized by adding 50 gm. of anhydrous sodium acetate to the mixture and the mixture is stirred for 30 minutes. The reflux condenser is replaced with a distillation head and the reaction mixture is heated to 50° C. A fraction weighing 703 gms. is obtained. This fraction is essentially pure isoprene.

The pressure is reduced to 100 mm. Hg and the temperature of the reaction mixture is held at 50° C., and a fraction weighing 545 gms. is obtained. This mixture consists of 235 gms. (43%) of acetic acid and 310 gms. (57%) of isoprene.

The pressure is reduced to 3 mm. Hg and the temperature of the reaction mixture is held at 50° C. A fraction weighing 2,462 gms. is obtained. This fraction con-

sists of 2,157 gms. (87.6%) of acetic acid and 305 gms. (12.4%) of prenyl acetate.

The pressure is held at 3 mm. Hg and the temperature of the reaction mixture slowly raised to 200° C. A fraction weighing 942 gms. is obtained. The residue weighs 256 gms.

The residue comprises a mixture of C₂₀ to C₇₅ polyisoprenoid hydrocarbons and a mixture of C₂₀ to C₇₅ polyisoprenoid acetates, in which the acetate portion of the mixture represents about 70 percent by weight.

EXAMPLE II.—Preparation of polyisoprenoid alcohol

To a solution of 1600 gms. of potassium hydroxide in 6280 gms. methanol is added at reflux 5000 gms. of the residue containing polyisoprenoid acetate made as in Example I (acid content: 0.015, ester content: 1.19, alcohol content: 0.104). The mixture is refluxed for an additional four hours, cooled to room temperature, neutralized with 1900 ml. of concentrated hydrochloric acid washed twice with 8 liters of a 5% sodium chloride solution, the water being subsequently extracted with 10 liters of petroleum ether, dried over magnesium sulfate and filtered. The petroleum ether is recovered under vacuum. Crude material in the amount of 4571 gms. is obtained (acid content: 0.06, ester content: 0.06, alcohol content: 0.95). The crude is then molecularly distilled. About 3548 gms. of material containing about 70% C₂₀-C₇₅ polyisoprenoid alcohols, and 30% C₂₀-C₇₅ polyisoprenoid hydrocarbons is obtained.

EXAMPLE III.—Preparation of lactic acid ester of polyisoprenoid alcohol

A mixture of 971 gms. of polyisoprenoid alcohol made in accordance with the procedure of Example II, 101 gms. of ethyl lactate, 10 gms. of sodium methylate, and 2000 gms. of toluene are heated and the methanol/ethanol-toluene azeotropes are distilled off for a period of 8 hours. The reaction mass is then cooled, acidified with acetic acid, and washed to neutrality with water and dilute sodium bicarbonate solution. The toluene is recovered under vacuum. About 976 gms. of crude reaction product is obtained and 480 gms. of this crude product is washed three times with water and dried to obtain the lactic acid ester of polyisoprenoid alcohol (acid content: 0.01, ester content: 0.38, alcohol content: 0.86). Another 480 gms. of the crude product is molecularly distilled to obtain the fractions listed below at the temperatures and pressures shown.

Fraction number	Rotor temperature, ° C.	Vacuum (microns-Hg)
1.....	56	55
2.....	65	33
3.....	66	28
4.....	68	23
5.....	69	18
6.....	73	16
7.....	80	16
8.....	84	14
9.....	90	14
10.....	102	13
11.....	103	12
12.....	106	12
13.....	113	12
14.....	120	12

A total of 413 gms. of material is obtained. The indicated fractions test as follows:

Fraction number	Acid content	Ester content	Alcohol content
2.....	.002	.24	1.02
5.....	.002	.20	0.98
8.....	.008	.33	1.03
11.....	.010	.54	0.91
14.....	.012	.36	0.69

EXAMPLE IV.—Preparation of lactic acid ester of polyisoprenoid alcohol

A mixture of 971 gms. of polyisoprenoid alcohol made in accordance with the procedure of Example II, 303

gms. ethyl lactate, 30 gms. sodium methylate, and 2000 gms. toluene is heated and the methanol/ethanol-toluene azeotrope is distilled off during a period of 9 hours. The reaction mass is then worked up as in Example III and 1085 gms. of crude is obtained. About 500 gms. of the crude is washed three times with water and dried to obtain the lactic acid ester of polyisoprenoid alcohols (acid content: 0.01, ester content: 1.18, alcohol content: 0.83). Another 500 gms. of the crude reaction product is molecularly distilled under reduced pressure to obtain the fractions indicated below at the temperatures and pressures shown:

Fraction number	Rotor temperature, ° C.	Vacuum (microns-Hg)
1.....	60	55
2.....	66	38
3.....	70	27
4.....	72	24
5.....	75	22
6.....	77	18
7.....	84	16
8.....	89	14
9.....	96	14
10.....	102	14
11.....	110	14
12.....	116	18
13.....	120	24

A total of 432 gms. of material is obtained. The indicated fractions test as follows:

Fraction number	Acid content	Ester content	Alcohol content
2.....	0.001	1.07	0.69
4.....	0.001	0.76	0.82
6.....	0.002	0.81	0.86
8.....	0.004	1.02	0.91
10.....	0.005	1.40	0.96
12.....	0.008	1.65	1.04
13.....	0.007	1.42	0.97

EXAMPLE V.—Preparation of lactic acid ester of polyisoprenoid alcohol

A mixture of 971 gms. of polyisoprenoid alcohol made in accordance with the procedure of Example II, 909 gms. of ethyl lactate, 90 gms. of sodium methylate, and 5000 gms. of toluene is heated, and the methanol/ethanol-toluene azeotrope is distilled off for a period of 11½ hours. The reaction mass is then worked up as in Example III. About 1220 gms. of crude is obtained, and 600 gms. thereof is washed three times with water and dried, and the lactic acid ester of polyisoprenoid alcohols is obtained with acid content: 0.003, ester content: 2.08, alcohol content: 0.93. Another 600 gms. of the crude is molecularly distilled under reduced pressure to obtain the fractions indicated at the temperatures and pressures shown:

Fraction number	Rotor temperature, ° C.	Vacuum (microns-Hg)
1.....	58	65
2.....	70	50
3.....	73	36
4.....	76	30
5.....	78	22
6.....	82	19
7.....	89	19
8.....	94	14
9.....	110	13
10.....	110	14
11.....	116	13
12.....	120	13
13.....	129	20
14.....	134	22
15.....	136	23

A total of 504.5 gms. of material is obtained. The indicated fractions test as follows:

Fraction number	Acid content	Ester content	Alcohol value
2.....	.006	3.13	1.05
4.....	.007	2.02	.64
6.....	.006	1.80	.75
8.....	.005	1.82	.84
10.....	.006	2.14	.86
12.....	.011	2.30	.98
14.....	.020	2.22	.81

EXAMPLE VI.—Preparation of lactic acid ester of polyisoprenoid alcohol

A mixture of 303 gms. of lactic acid, 150 gms. of benzene and 4.4 gms. of concentrated sulfuric acid is refluxed through a Bidwell trap and the aqueous layer withdrawn until liberation of water ceases. Then 408 gms. of polyisoprenoid alcohol made in accordance with the procedure of Example II is added and the reaction mass further refluxed with water removal continued until liberation of water again ceases. The mass is washed to neutrality with water and dilute sodium bicarbonate solution to obtain 392 gms. of crude lactic acid esters of polyisoprenoid alcohol. About 380 gms. is molecularly distilled under reduced pressure and the fractions noted are obtained at the temperatures and pressures shown:

Fraction number	Rotor temperature, ° C.	Vacuum (microns-Hg)
1 -----	70	75
2 -----	69	60
3 -----	77	45
4 -----	86	35
5 -----	97	28
6 -----	106	23
7 -----	121	19
8 -----	136	16

A total of 259 gms. of material is obtained. The indicated fractions test as follows:

Fraction Number	Acid content	Ester content	Alcohol content
1 -----	.01	0.18	0.05
3 -----	.01	0.17	0.06
5 -----	.01	0.28	0.08
7 -----	.01	0.44	0.16
8 -----	.01	0.69	0.22

EXAMPLE VII.—Tobacco flavor enhancing

A series of tobacco blends is prepared by spraying a solution of each of the agents shown in the following tabulation in equal parts by weight of acetone and denatured ethyl alcohol onto a tobacco blend consisting of 55% by weight of Type 12 Virginia tobacco and 45% by weight of burley tobacco. The agent is applied to the tobacco blend at a level of 1% by weight based on the weight of tobacco. Each of the sprayed tobacco blends is air dried, made into cigarettes, and conditioned by holding overnight. The cigarettes are evaluated by organoleptic testing wherein they are smoked by a test panel and their smoking characteristics determined by sensory methods.

Flavoring agent employed	Evaluation comment
Untreated control -----	Good taste, but harsh.
Fraction 13 of Example IV -----	Milder—good taste.
Fraction 14 of Example V -----	Strong tobacco taste—mild-smooth.
Fraction 3 of Example VI -----	Smoother improved flavor.
Lactate ester of polyisoprenoid alcohols of Example VI.	Smoother, milder taste.

EXAMPLE VIII

In accordance with the procedure described in Example VII, comparison tests are made among cigarettes made from a control (untreated), a sample treated with 1% by weight of a mixture of 40% lactic acid and 60% polyisoprenoid alcohol, and a sample treated with 1% by weight of fraction 14 of the lactate ester of polyisoprenoid alcohol of Example V. The tobacco used in the test cigarettes was a 45–55 blend of burley and Virginia tobaccos.

The test smokers reject the samples treated with the lactic acid-polyisoprenoid mixture as having a floral-per-

fumey-alien taste. Cigarettes made from tobacco treated with the lactate ester fraction of polyisoprenoid alcohols are preferred over the control.

EXAMPLE IX

Using the techniques described in Example VII, a comparison is made among cigarettes made from untreated tobacco (control), tobaccos treated with fraction 14 of the lactic acid ester of polyisoprenoid alcohol of Example V and tobaccos treated with lactic acid. In each case 1% by weight of the flavoring agent is added to a 45–55 blend of burley and Virginia tobaccos. Although the lactic acid-treated tobaccos smoke smoother than the control, no enhancement in flavor over the control is detected. The cigarettes made from tobaccos treated with the lactic acid esters of polyisoprenoid alcohols not only are found to smoke smoother than the control but the esters also retain and enhance the flavor of the cigarette.

EXAMPLE X

Application in small amounts by weight of the lactic acid esters of polyisoprenoid alcohols to tobacco-products utilizing cigar stems and various tobacco substitutes upon organoleptic testing is found to reduce the otherwise harsh, acrid, woody taste of such tobacco products.

EXAMPLE XI.—Preparation and evaluation of lactate esters of polyisoprenoid alcohols

A mixture of 242.7 gms. saponified polyisoprenoid acetate residue (acid content: nil, ester content: 0.025, alcohol content: 1.03), 75.7 gms. ethyl lactate, 7.5 gms. sodium methylate and 500 gms. toluene is heated and the methanol/ethanol-toluene azeotrope distilled off over a period of 3¼ hours. The reaction mass is then cooled, acidified with acetic acid, and washed to neutrality with water and dilute sodium bicarbonate solution. The toluene is recovered under vacuum. About 253 gms. of crude is obtained (acid content: 0.002, ester content: 1.40, alcohol content: 0.88). About 245 gms. of crude is distilled under reduced pressure and 180.6 gms. is obtained. The fractions obtained at the indicated rotor temperatures on the molecular still tested as shown below:

Fraction number	Acid content	Ester content	Alcohol content	Rotor temp.	Vacuum, microns-Hg
2 -----	.001	0.34	0.48	63	32
4 -----	.002	0.47	0.84	69	22
6 -----	.002	0.65	0.94	72	15
8 -----	.004	0.91	0.87	78	13
10 -----	.005	1.57	1.18	90	13
12 -----	.009	2.60	1.47	87	13

Fractions 1–6 are combined (86.9 gms.; acid content: 0.003, ester content: 0.44, alcohol content: 0.73) and fractions 7–12 are combined (93.7 gms., acid content: 0.007, ester content: 1.28, alcohol content: 1.01).

The foregoing material is representative of esters obtained by reacting a ½ molecular ratio of alcohol to lactic acid. The low-boiling section is found to improve the taste and sidestream odor of stems, black tobacco, and reconstituted tobacco sheet. The high-boiling section tends to smooth out the harshness of heavy, harsh cigarette tobaccos and gives more body and enhanced flavor to low-grade and mild tobaccos.

EXAMPLE XII

A mixture of 242.7 gms. of the saponified polyisoprenoid alcohol residue of Example XI, 227.2 gms. ethyl lactate, 22.5 gms. sodium methylate, and 1250 gms. toluene is heated, and the methanol/ethanol-toluene azeotrope distilled off over a period of 3¼ hours. The reaction mass is then cooled, acidified with acetic acid, and washed neutral with water and dilute sodium bicarbonate solution. The toluene is removed under vacuum. About 286 gms. of crude is obtained (acid content: 0.004, ester content:

2.87, alcohol content: 1.10), and 276 gms. of crude is distilled under reduced pressure, and 215.5 gms. of product is obtained. The fractions obtained at the indicated rotor temperature tested as shown below:

Fraction number	Acid content	Ester content	Alcohol content	Rotor temp.	Vacuum, microns-Hg
2 -----	.001	2.09	0.63	63	25.3
4 -----	.001	1.57	0.79	69	26.0
6 -----	.001	1.69	0.92	78	21.0
8 -----	.001	2.14	1.07	90	18.0
10 -----	.001	3.15	1.28	102	15.0

Fractions 1-4 are combined (95.5 gms., acid content: 0.006, ester content: 2.05, alcohol content: 1.05) and fractions 5-11 are combined (120.0 gms., acid content: 0.01, ester content: 2.27, alcohol content: 1.20).

The foregoing material is representative of esters obtained by reacting a 1/9 molecular ratio of alcohol to lactic acid. The low-boiling section is found to be excellent in improving the taste and sidestream odor of stems, black tobacco, and reconstituted tobacco sheet. The high-boiling section is found to be excellent in smoothing out the harshness of heavy, harsh cigarette tobaccos and in enhancing the flavor of mild and low-grade tobaccos.

EXAMPLE XIII

A mixture of 242.7 gms. of saponified polyisoprenoid alcohol residue of Example XI, 454.4 gms. ethyl lactate, 45.0 gms. sodium methylate and 2500 gms. toluene are heated and the methanol/ethanol-toluene azeotrope distilled off over a period of 8½ hours. The reaction mass is then cooled, acidified with acetic acid, and washed neutral with water and dilute sodium bicarbonate. The toluene is recovered under vacuum. About 373 gms. of crude is obtained (acid content: 0.009, ester content: 4.74, alcohol content: 1.39), 363 gms. of crude is distilled under reduced pressure, and 279.5 gms. of product is obtained. The fractions obtained at the indicated rotor temperatures test as shown below:

Fraction number	Acid content	Ester content	Alcohol content	Rotor temp.	Vacuum, microns-Hg
2 -----	.002	3.92	1.26	60	30
4 -----	.002	3.07	1.07	67	18
6 -----	.004	2.87	0.89	74	16
8 -----	.002	3.10	0.95	78	10
10 -----	.003	3.88	1.31	96	9
12 -----	.005	5.22	0.85	110	9
14 -----	.005	6.42	1.20	118	8

Fractions 1-6 are combined (135.0 gms., acid content: 0.007, ester content: 3.56, alcohol content: 1.37) and fractions 7-14 are combined (144.5 gms., acid content: 0.008, ester content: 4.08, alcohol content: 1.31).

The foregoing material is representative of esters obtained by reacting a 1/18 molecular ratio of alcohol to lactic acid. The low-boiling section is very good in improving the taste and sidestream aroma of stems, black tobacco, and reconstituted tobacco sheet. The high-boiling section is very good in smoothing out the harshness of heavy, harsh cigarette tobaccos and in enhancing the flavor of mild and low-grade tobaccos.

EXAMPLE XIV

A mixture of 239 gms. of polyisoprenoid ester residue (acid content: 0.015, ester content: 11.19, alcohol content: 0.104), 227.2 gms. ethyl lactate, 22.7 gms. sodium methylate, and 1250 gms. n-hexane is heated at 70 to 72° C. and the methanol-, ethanol-, and ethyl acetate/hexane azeotropes distilled off over a period of nine hours. The reaction mass is then cooled, acidified with acetic acid, and washed to neutrality with water and dilute sodium bicarbonate. The hexane is recovered under vacuum.

About 255 gms. of crude is obtained (acid content: 0.02, ester content: 2.61, alcohol content: 0.87) and 240 gms. of this is distilled under reduced pressure. 160 gms. of

product is obtained. The fractions obtained at the following rotor temperatures test as shown below:

Fraction number	Acid content	Ester content	Alcohol content	Rotor temp.	Pressure, microns-Hg
2 -----	Nil	2.91	0.72	64	32
4 -----	Nil	2.59	0.63	67	15
6 -----	Nil	2.37	0.60	79	10
8 -----	Nil	2.44	0.69	85	8
10 -----	Nil	2.56	0.72	95	6
12 -----	Nil	2.71	0.73	111	6

Fractions 1-7 were combined (140.5 gms., acid content: 0.004, ester content: 0.12, alcohol content: 0.11), and fractions 8-15 were combined (130.2 gms., acid content: 0.01, ester content: 0.49, alcohol content: 0.09).

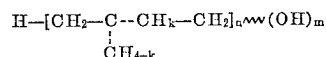
The material of this example improves the flavor of various cigarette tobaccos.

The alcohol of Example II shows IR absorption at 10.0μ indicating about ½ mole of primary allylic hydroxyl per mole of alcohol (based on a molecular weight of 550-600) and 8.6-8.9μ absorption indicating tertiary hydroxyls. This alcohol shows UV absorption at 240 and 280 mμ, the 240 mμ absorption indicating about 0.2-0.3 mole of conjugated dienoid material per mole based on above molecular weight. The lactate of Example XII shows similar UV absorption.

The invention in its broader aspects is not limited to the specific steps, processes, compositions, combinations and improvements described, but departures may be made therefrom within the scope of the accompanying claims and their equivalents without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. A lactic acid ester of a polyisoprenoid alcohol wherein the polyisoprenoid alcohol is represented by the formula



where m is one or two, n is an integer of from about 4 to about 15, each dotted line is a bond selected from the group consisting of a single bond and a double bond, one double bond being present in a non-tertiary hydroxyl-containing isoprenoid unit, and k is an integer of from 1 to 2, the value of k being determined by the presence of said double bond.

2. The lactic acid ester of claim 1 wherein at least one molecular proportion of lactic acid is present for each molecular proportion of polyisoprenoid alcohol.

3. The lactic acid ester of claim 1 wherein the lactic acid is present in from about 3 to about 25 molecular proportions for each molecular proportion of polyisoprenoid alcohol.

4. The lactic acid ester of claim 1 wherein the lactic acid is present in an amount of from about 6 to about 18 molecular proportions for each molecular proportion of polyisoprenoid alcohol.

5. The lactic acid ester of claim 1 containing about 9 molecular proportions of lactic acid for each molecular proportion of polyisoprenoid alcohol.

6. The lactic acid ester of claim 1 having an acid content of from nil to about 0.045, an alcohol content of from about 0.4 to about 2.5, and an ester content of from about 0.3 to about 7.5.

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