

[54] TOBACCO COMPOSITIONS COMPRISING MONO-ESTERS OF MONO- AND DIALKYL MALONATES

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[51] Int. Cl. A24b 15/04

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

[56] References Cited UNITED STATES PATENTS

2,766,145	10/1956	Jones	131/17 R
3,095,882	7/1963	Hind et al.....	131/17 R
3,782,391	1/1974	Means et al.....	131/17 R

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[57] ABSTRACT

An article of manufacture comprising tobacco and a small but effective amount of one or a mixture of monoesters of mono- and/or di-alkylmalonates as a flavorant composition. The indicated malonates decompose during smoking of the tobacco by decarboxylation to give the corresponding alkanoate esters which improve the taste and aroma of tobacco smoke. For example, monoethyl sec-butylmalonate in a cigarette at a level of about one ppm on the tobacco will produce a smoke flavor characterized by a fermented apple-peel with an English walnut-like taste. The flavor and taste apparently arise from the conversion of the monoethyl sec-butylmalonate to ethyl β-methylvalerate.

9 Claims, No Drawings

TOBACCO COMPOSITIONS COMPRISING MONO-ESTERS OF MONO- AND DIALKYL MALONATES

BACKGROUND

It has long been known in the tobacco art that domestic tobaccos such as burley, Maryland and bright leaf or Virginia are low in natural flavor compared to the so-called oriental or aromatic tobaccos which are imported from Turkey, Greece, and other countries. Those aromatic tobaccos contain natural materials in their composition which said materials give those tobaccos characteristic aroma and flavor. In order to produce more flavorful tobacco products, it has long been the usual practice in the United States tobacco industry to either blend domestic and oriental tobaccos and/or add synthetic or natural additives to domestic tobacco blends. These techniques provide cigarettes and other tobacco products which possess desired flavor and aroma characteristics.

In copending U.S. patent application Ser. No. 127,792, by Means, Kallianos and Tenney, filed Mar. 24, 1971 now U.S. Pat. No. 3,782,391 issued Jan. 1, 1974, improved tobacco compositions are disclosed which comprise flavoring-agents selected from the group consisting of C₁ - C₆ alkyl esters and β-phenethyl esters of β-methylvaleric acid. These agents impart to the tobacco and its smoke a fruity apple-like aroma and a nut-like flavor. However, the valerates, such as ethylβ-methylvalerate, are relatively volatile substances with low odor threshold values which make them difficult substances to use in flavoring tobacco because of the problem of evaporation on prolonged storage of the treated tobacco.

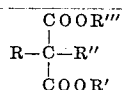
It is therefore an object of the present invention to provide tobacco compositions having improved flavoring agents.

Another object of this invention is to provide relatively non-volatile flavoring agents for tobacco which are stable during storage and upon smoking of the tobacco provide a pleasant aroma and taste.

These and other objects are set forth in greater detail in the accompanying specification.

THE INVENTION

This invention is directed to tobacco compositions comprising a small but effective amount of at least one monoester of mono- and di-alkylmalonates having the formula



wherein R, R' are independently selected from the group consisting of straight or branched-chain alkyl, and aralkyl radicals having from one to eight carbon atoms, and R'' is either hydrogen or lower alkyl radical having from one to six carbon atoms and R''' is hydrogen or alkali or alkaline earth metal.

A preferred embodiment of the present invention is a tobacco composition comprising monoethyl sec-butylmalonate. This compound is synthesized by procedures which have been published in the chemical literature. Specifically, monoethyl sec-butylmalonate is pre-

pared by hydrolysis of diethyl sec-butylmalonate with one equivalent of potassium or sodium hydroxide. The diethyl sec-butylmalonate can be obtained by the reaction of diethyl malonate with 2-bromobutane in the presence of a base such as sodium ethoxide. Similarly other alkyl, or aralkyl substituted malonate diesters can be obtained by the reaction of dialkyl malonate with the desired haloalkane, such as bromoalkane, in the presence of a base such as sodium ethoxide. R'' substitution may be achieved by reaction of the corresponding alkyl substituted malonate diester with sodium and the sodium derivative reacted with the desired alkyl halide.

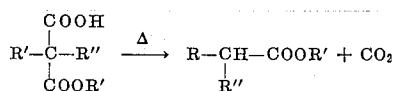
The salts of the monoesters of the substituted malonic acids may also be used according to this invention. These can be prepared by reaction of the appropriate malonate half-ester with an equivalent amount of a hydroxide or carbonate of the alkali or alkaline earth metals. Use of basic ion-exchange resins may also accomplish the desired results.

It will be readily apparent to those experienced in the art that the above methods of preparation are intended only to be illustrative and that the products may be obtained by other chemical methods.

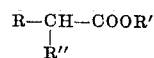
The compounds of this invention are useful to modify the flavor of smoked tobacco products and are especially useful as cigarette and pipe tobacco flavorants. They may be applied to tobacco or reconstituted tobacco sheet or to cigarette paper by spraying in a suitable solvent such as ethanol, propylene glycol, glycerine, or casing solution, by dipping into a solution containing the product, or by incorporation into a flavor formulation normally applied to tobacco, reconstituted tobacco sheet or cigarette paper. The concentration of flavorants may vary from 0.00001 to 0.1 percent by weight of tobacco or tobacco product although higher and lower concentrations may be employed if desired.

It should be appreciated that the compounds of the present invention are not flavorants per se, but decompose when heated to give flavorant alkyl alkanates. Low molecular weight alkyl alkanate esters are relatively volatile and generally highly aromatic substances with very low odor threshold values. These properties limit their usefulness as tobacco flavorants because of the problem of evaporation on prolonged storage of the treated tobacco.

Monoesters of mono- and di-alkylmalonates, on the other hand, are relatively non-volatile, non-odorous, and stable on tobacco during manufacture and storage but decompose thermally during the smoking to give high yields of the flavorant alkyl alkanate esters. The liberation of the flavorant esters from the compounds of the present invention during smoking, can be accounted for by the decarboxylation reaction depicted below:



wherein



is the active flavorant alkanate ester.

Reactions analogous to this are well documented in the chemical literature (Fieser, L. F. and Fieser, M. "Advanced organic Chemistry." 1961. p.449. Reinhold Publishing Corporation, New York.).

More specifically, monoethyl sec-butylmalonate decomposes during the smoking of tobacco to release ethyl β -methylvalerate. The use of the latter compound in tobacco composition is disclosed in the above-noted copending patent application, Ser. No. 127,792. However, ethyl β -methylvalerate is a relatively volatile substance with a low odor threshold value making it difficult substance to use in flavoring tobacco because of the problem of evaporation on prolonged storage of the treated tobacco.

The monoethyl sec-butylmalonate, on the other hand, is non-volatile, non-odorous, and stable on tobacco during manufacture and storage but decomposes during smoking to give high yields of ethyl β -methylvalerate.

The present invention offers economic advantages as well in that no loss due to volatilization of material during application and storage is incurred.

The preparation and use of monoesters of mono- and di-alkyl malonates are illustrated by the following examples.

EXAMPLE I

Diethyl sec-Butylmalonate

This compound was prepared according to the procedure in Organic Syntheses (Organic Syntheses, Coll. Vol. III, 495 (1955)).

A 250-ml, 3-necked flask equipped with a condenser was charged with 70 ml anhydrous ethanol and 3.5g (0.152 moles) of sodium. The last amounts of sodium were dissolved by warming the flask on a steam bath. A stirrer and dropping funnel were then attached to the flask. The latter was warmed on a steam bath and 25 g (0.156 m) of diethyl malonate was added in a steady stream with stirring. After a few minutes additional stirring, 21 g (0.153 m) of 2-bromobutane was rapidly added with stirring and warming. The reaction mixture was stirred and refluxed for 48 hours.

The ethanol was distilled directly from the reaction flask. Twenty ml. of water was added to the cooled mixture, the layers were separated, and the organic layer was distilled. The product was collected at 112°-119°/20-25mm; yield 23.9 g (72%); $\lambda_{max}^{CCl_4}$ 5.70 and 5.76 μ .

EXAMPLE II

Monoethyl sec-Butylmalonate

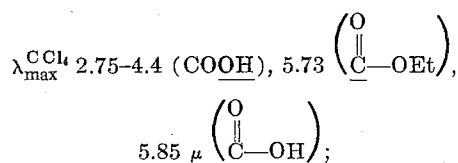
This compound was synthesized according to a slightly modified published procedure (Organic Syntheses, Coll. Vol. IV, 417 (1963)).

Diethyl sec-butylmalonate (13.5 g, 0.0625 m) and 40 ml. of absolute ethanol were placed in a 250-ml, 3-necked flask equipped with a stirrer, condenser, and dropping funnel. A solution of 3.5 g (0.0625 m) of potassium hydroxide in 40 ml. ethanol was added dropwise at room temperature over a period of 1 hour. After 2 hours additional stirring, the reaction mixture was allowed to stand overnight.

The ethanol solution (containing a small amount of white precipitate) was cooled to 0° and neutralized by

addition of 5.2 ml concentrated hydrochloric acid. The mixture was filtered by gravity and the ethanol was removed on the rotary evaporator.

The product was dissolved in 50 ml. ether, cooled to 0°, and extracted with cold 5% sodium hydroxide solution. The ether layer from this extraction was washed with water and dried to give 3.4 g recovered diethyl sec-butylmalonate. The aqueous-sodium hydroxide extract was cooled to 0° and neutralized with concentrated hydrochloric acid. The resulting oil was taken up with ether and the ether layer was washed with water and dried to give 7.1 g of monoethyl sec-butylmalonate;



mass spectrum: no molecular ion; major peaks at m/e 143, 132, 115, 114, 104, 87, 86, 69, and 41.

EXAMPLE III

Monomethyl sec-Butylmalonate

Freshly cut sodium (1.5 g, 0.065 moles) was dissolved in 50 ml. of anhydrous methanol. The solution was cooled to room temperature and a solution of 4.5 g (0.024 m) of monoethyl sec-butylmalonate in 5 ml. methanol was added in one portion. The reaction solution was refluxed on a steam bath for 1 day.

The solution was cooled to 0°C and 4 ml. of concentrated hydrochloric acid was added dropwise with stirring. After evaporation of the methanol on the rotary evaporator, ether was added. The ether solution was washed sequentially with equal volumes of water, water containing 0.5 ml. saturated aqueous sodium bicarbonate solution, water, and saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate, and the solvent evaporated on the rotary evaporator to give 3.6 g colorless oil; $\lambda_{max}^{CCl_4}$ 2.75 - 4.4 (OH of COOH), 5.70 (C=O of ester), and 5.83 μ (C=O of acid). The NMR spectrum shows a methoxy singlet at 6.3 τ and the absence of absorption due to an ethoxy ester group. Mass Spectrum: no molecular ion; major peaks at m/e 118, 101, 100, 87, 69 and 41. Gas chromatographic analysis give a single peak having the same retention time as that of authentic methyl β -methylvalerate. Thermogravimetric analysis indicated decomposition to occur from about 110 to 160°C. The decomposition product possessed a sweet, apple, fruity aroma.

EXAMPLE IV

Diethyl methyl-n-propylmalonate

Freshly cut sodium (1.14 g, 0.0496 m) was dissolved in 50 ml. of anhydrous ethanol. The solution was warmed and 10g (0.0495 m) of diethyl n-propylmalonate was added with stirring over a period of 5-10 minutes. The reaction mixture was warmed and stirred an additional 15 minutes and allowed to cool to room temperature. Methyl iodide (9.6g, 0.0676 m) was

then added with stirring over a period of 3-4 minutes. The solution was then stirred and refluxed gently for 4.5 hours.

The solution was cooled and the ethanol and excess methyl iodide were removed on the rotary evaporator. Ether and water were added, the layers were shaken in a separatory funnel, and the aqueous layer was removed. The ether layer was washed with sodium thiosulfate solution, water, and saturated aqueous sodium chloride solution, dried over sodium sulfate, and concentrated on the rotary evaporator. The product was used in the following reaction, described in Example V, without purification; $\lambda_{max}^{CCl_4}$ 5.75 (C=O) and 8.03 μ (C-O). The NMR spectrum was consistent with the structure and the mass spectrum showed major peaks at m/e 174, 171, 143, 128, 115, 87, 69, 45 and 41.

EXAMPLE V

Monoethyl methyl-n-propylmalonate

To a solution of 10 g (0.0463 m) of diethyl methyl-n-propylmalonate, prepared as described in Example IV, in 30 ml. of ethanol was added dropwise with stirring at room temperature over a period of 0.75 hours a solution of 3.16 g (0.0563 m) of potassium hydroxide (minimum 85% assay) in 30 ml. ethanol. The solution was stirred for 3 days and maintained at room temperature.

The solution was cooled to 0° and 3.2 ml. of concentrated hydrochloric acid was added dropwise with stirring. The solids were removed by filtration and the ethanol was evaporated on the rotary evaporator. The product had $\lambda_{max}^{CCl_4}$ 2.7-4.4 (OH of COOH), 5.75 (C=O of -COOC₂H₅), and 5.83 μ (acid carbonyl). The NMR spectrum was consistent with the structure and thermogravimetric analysis indicated decomposition in the range 150°-200°. The decomposition product had an apple-fruity aroma. The mass spectrum showed an extremely weak molecular ion; major peaks at m/e 146, 143, 128, 115, 87, 69, 45, 41.

EXAMPLE VI

Monoethyl sec-Butylmalonate

To 25 g of n-octyl alcohol was added 1.1 g of sodium hydride (50% dispersion). After the sodium hydride had dissolved (about 1 hour stirring), 3 g monoethyl sec-butylmalonate was added in one portion. The mixture was stirred at 45°-50° for 6 hours, then at 25°-30° for 20 hours.

The mixture was cooled to 0° and 1.5 ml. of concentrated hydrochloric acid was added dropwise. Ether and water were added and the mixture was shaken in a separatory funnel. The ether layer was extracted twice with dilute sodium hydroxide solution and the combined aqueous layers were cooled and reacidified with concentrated hydrochloric acid. The aqueous layer was then extracted with ether and the ether layer was washed with a solution of 20 ml. water and 0.5 ml. saturated sodium bicarbonate solution followed by repeated washing with water. The ether layer was finally washed with saturated sodium chloride solution, dried over sodium sulfate, and evaporated on the rotary evaporator. The product was isolated by preparative thin-layer chromatography on silica gel GF-254 (250 μ thick) eluting with 50% ether-petroleum ether. The product exhibited $\mu_{max}^{CCl_4}$ 2.75-4.2 (OH of COOH), 5.73 (ester carbonyl), and 5.84 μ (acid carbonyl); NMR spectrum: 5.87 τ (triplet), 6.76 τ (doublet); mass

spectrum: weak M+ at m/e 272; major peaks at m/e 161, 143, 112, 105, 87, 71, 70, 69, 57, 56, 55, 43, 42, 41.

EXAMPLE VII

Calcium monoethyl sec-Butylmalonate

To a cooled solution of 2.5 g (0.0133 m) monoethyl sec-butylmalonate in 10 ml. 95% ethanol was added with stirring over about 2 minutes 0.492 g (0.00665 m) calcium hydroxide. The solution was maintained cool at 10° and stirred for an additional 10 minutes, at which time it became viscous. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 2.5 hours. Subsequently, the solvent was evaporated on the rotary evaporator. The infrared spectrum of the white powder product, when measured in KBr pellet, showed absorption maxima at 5.77, 5.84, 6.3, 7.17, 7.52, and 9.67 μ characteristic for a mixed ester salt of the type expected.

EXAMPLE VIII

Samples of a commercial blend of tobaccos were treated with several of the compounds of this invention at various levels of application. The treated tobaccos were manufactured into cigarettes and these were evaluated organoleptically by experienced flavor panels.

Cigarettes containing monoethyl sec-butylmalonate in the tobacco at levels of 0.5, 1, 10, and 25 ppm, were judged to produce a smoke flavor characterized by a fermented apple-peel and English walnut-like taste. The intensity of the aroma, flavor and taste effects increased with increasing levels of the additive in the cigarettes and at levels above 10 ppm, the effects were described as being overpowering.

Cigarettes containing monoethyl methyl-n-propylmalonate at a level of 25 ppm in the tobacco were judged to deliver a heavy walnut flavor and aroma to the smoke.

Cigarettes containing tobacco treated with monoethyl sec-butylmalonate at 100 ppm produced a smoke described as having a sweet, apple-cider and walnut-like taste. The side-stream smoke aroma of the cigarettes was described as a sweet, "winey-walnut" complex.

The sweet, apple, walnut-like complex aromas described herein are not due to the mono-esters of the malonates of this invention, but rather to the alkyl alkananoate esters emanating from their thermal decarboxylation. These aromas are found in the smoke of the treated cigarettes not only immediately after treatment of the tobacco, but also after several months of age, without any noticeable diminution in the levels of taste. This cannot be achieved by the simple addition of alkyl alkananoate esters of the type that are useful as flavorants on tobacco.

The flavorant alkyl alkananoate esters themselves are much too volatile to remain on the tobacco during the prolonged shelf storage experienced by packaged tobacco products.

The superior stability and tenacity of the compounds of the present invention on tobacco over alkyl alkananoate esters is best illustrated by the following example.

EXAMPLE IX

A 10 g sample of a commercial blend of cased and cut tobaccos, containing 9.1 mg of added ethyl β

-methylvalerate, was placed in an empty desiccator (A). In the center of the desiccator was placed a small Petri dish containing 5 ml squalene. In a similar manner, a 12 g sample of the same tobacco blend, which in this instance contained 52.2 mg of added monoethyl sec-butylmalonate, was placed in desiccator (B). A Petri dish with 5 ml. of squalene was placed in this desiccator as well. The desiccators were covered tightly and stored side by side on a lab bench. The squalene samples were monitored periodically for ethyl β -methylvalerate content by suitable gas chromatographic techniques. One would expect ethyl β -methylvalerate to transfer from the tobacco into the squalene by volatilization and solubilization.

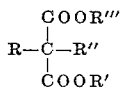
Using the above procedure, we found that ethyl β -methylvalerate is so volatile that the tobacco in desiccator (A) had lost 98 percent of the added material after 10 days of storage, as calculated from the presence of 8.9 mg of ethyl β -methylvalerate in the squalene of that desiccator. The squalene in desiccator (B) was essentially void of any ethyl β -methylvalerate. That the monoethyl sec-butylmalonate was still present on the tobacco undecomposed, was ascertained by extraction of the tobacco with ether, low temperature pyrolysis of the extract after evaporation of the ether, and gas chromatographic analysis of the pyrolysate for ethyl β -methylvalerate. In this case, more than 99 percent of the monoethyl sec-butylmalonate was present undecomposed on the tobacco even after 26 days of storage. Yet this malonate could be decarboxylated to yield ethyl β -methylvalerate by allowing the tobacco to burn.

In another experiment, we found that the calcium salt of monoethyl sec-butylmalonate showed stability similar to the free acid.

It will be appreciated that while several embodiments of this invention are shown above, the invention is not to be limited thereto, since many modifications will be obvious to those skilled in the art. Accordingly, such modifications are to be contemplated within the spirit of the invention as disclosed and claimed herein.

We claim:

1. Tobacco smoking compositions comprising tobacco and a small but effective amount of at least one monoester of mono- and di-alkylmalonates having the formula:



wherein R, R' are independently selected from the group consisting of straight or branched-chain alkyl

and aralkyl radicals having from one to eight carbon atoms, R'' is either hydrogen or lower alkyl radical having from one to six carbon atoms, and R''' is hydrogen or an alkali or alkaline earth metal.

2. The composition of claim 1 wherein said malonate is monoethyl sec-butylmalonate.

3. The composition of claim 1 wherein said malonate is monomethyl sec-butylmalonate.

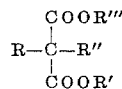
4. The composition of claim 1 wherein said malonate is monoethyl methyl-n-propylmalonate.

5. The composition of claim 1 wherein said malonate is monooctyl sec-butylmalonate.

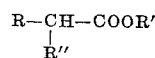
6. The composition of claim 1 wherein said malonate is calcium monoethyl sec-butylmalonate.

7. The composition of claim 1 wherein said malonate comprises from about 0.00001 to about 0.1 percent by weight based on the weight of said tobacco.

8. A process for the preparation of a tobacco smoking composition which comprises applying to tobacco a small but effective amount of a relatively non-volatile, non-odorous and stable flavoring agent of mono-esters of mono- and di-alkylmalonates having the formula:



wherein R, R' are independently selected from the group consisting of straight or branched-chain alkyl and aralkyl radicals having from two to eight carbon atoms, R'' is either hydrogen or lower alkyl radical having from one to six carbon atoms, and R''' is hydrogen or an alkali or alkaline earth metal wherein said malonate thermally decomposes during smoking to yield a low molecular weight alkanooate ester of the formula:



where R, R' and R'' are as defined above.

9. A process according to claim 8 wherein said malonate is applied to said tobacco in a range from about 0.00001 to about 0.1 percent weight based on the weight of said tobacco.

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