ABSTRACT OF THE DISCLOSURE

An improved smoking tobacco containing a substantially involatile propenyl ketone or carboxylic ester, formed by reacting a carboxylic acid and a beta-keto-alcohol, as flavor improving agents.

This invention concerns improvements relating to smoking tobacco. It seeks to improve the flavour of the smoke derived from such tobacco.

Substances are known which can be added to tobacco to improve the flavour of the smoke, such as menthol and liquorice, and it is a characteristic of most such substances that they have strong individual flavours. Considerable care and skill is required in applying these substances, or blends thereof, to give a required improvement to the flavour of the smoke of the treated tobacco. Generally, they act mainly by adding their individual flavour characteristics to those already present in the smoke, but the resultant alteration of flavour is not always desirable and may even render the smoke from the treated tobacco unacceptable.

The present invention therefore seeks to add to tobacco substances which, when released by the heat generated by the burning tobacco, have little or no individual flavour and therefore contribute, at most, only slightly to the smoke flavour, but which serve to modify or improve the characteristic flavour of the tobacco itself rather than to add another flavour characteristic.

According to the invention, the characteristic flavour of tobacco smoke is modified or improved by the addition of one or more propenyl ketones to cut tobacco. Propenyl ketones suitable for the purpose have the general formula R.COO.CH.CH.CH₃, where R is a normal-, iso- or tertiary alkyl or cycloalkyl radical, especially the methyl, ethyl, isopropyl, tertiary-buty1 and cyclohexyl propenyl ketones. While many of these ketones can be effectively added directly to the tobacco, some are rather volatile. In the latter case, to avoid premature loss during smoking or storage, the desired ketone is advantageously added to the tobacco in the form of a substantially involatile compound which can break down to yield the ketone under the influence of the heat produced on the smoking of the tobacco. Such compounds are the carbonyl esters of keto-alcohols corresponding to the un-saturated ketones.

Accordingly, it is proposed to add to cut tobacco an involatile carboxylic ester of a beta-keto-alcohol corresponding to a propenyl ketone, i.e. an alcohol of the form R.CO.CH₂.CH(OH).CH₃.

The concentration on the tobacco of a ketone, or of an involatile ester which can yield the ketone, may be between 0.1 and 2,000 micrograms per gram of tobacco. However, the optimum range is believed to be between 0.1 and 200 micrograms.

The ketones or esters can be added to the cut tobacco in various ways, for example by spraying or dipping or by evaporation into a closed container inside which the tobacco is tumbled. This last method is suitable for the methyl, ethyl and isopropyl ketones. The required amount of the ketone is applied to a wick fixed to a wall of the container, whose surface is heated to a controlled temperature of not more than 80°C, appropriately. The addition of the ketone to the tobacco generally requires fifteen minutes to one hour depending upon the volatility of the ketone. The same method can be used also with less volatile ketones, for example cyclohexyl ketone which, because of the intensity of its effect, is applied in very small amounts. For the esters, spraying the tobacco with a solution in diethyl ether or acetone is suitable.

Examples of the preparation and use of two suitable ketones and of methods of preparation of esters will now be described:

EXAMPLE I.—METHYL PROPENYL KETONE

4-hydroxy pentan-2-one (25 ml.) was heated under reflux with crystalline oxalic acid (1 gm.) for 1 hour. The product was distilled to give a two-layer distillate which was separated. The lower aqueous layer was extracted successively with three portions (each of 10 ml.) of diethyl ether. The extracts were combined with the upper layer and the resulting solution was dried over anhydrous sodium sulphate.

Pure methyl propenyl ketone was isolated by gas-chromatographic separation using a column of diglycerol supported on "Celite" (a diatomaceous earth) at 100°C, using hydrogen as the carrier gas.

A blend of flue-cured cut cigarette tobacco was treated with the methyl propenyl ketone, using an addition of 50 micrograms per gram of tobacco, and was made into cigarettes. The ketone was applied by the evaporation method described above. Using similar cigarettes made from the same, but untreated, tobacco as a control, the treated and untreated cigarettes were compared by an experienced smoking panel. The treated cigarettes were strongly preferred, and tests using higher concentrations of the ketone showed that it was acceptable up to concentrations of 2,000 micrograms per gram of tobacco.

EXAMPLE II.—ETHYL PROPENYL KETONE

Ethyl bromide (30 gm.) in anhydrous diethyl ether was added dropwise to magnesium turnings (6.6 gm.) and a crystal of iodine in anhydrous diethyl ether (150 ml.) at 24°C., to give a solution of a Grignard-type reagent, namely ethyl magnesium bromide.

A solution of crotonaldehyde (36.6 gm.) in anhydrous diethyl ether (100 ml.) was added slowly to the reagent. The reaction product formed was hydrolysed by pouring it, with stirring, into a mixture of 10% aqueous sulphuric acid solution and ice. The ethereal solution was separated and dried over anhydrous sodium sulphate. The ether was removed under partial vacuum in a rotary evaporator.

The residue, 2-hexen-4-ol, was dissolved in acetone (50 ml.) and cooled to —15°C. Chromic acid reagent was prepared from chromic oxide (16 gm.), concentrated sulphuric acid (14 ml.) and water (50 ml.) and was cooled in ice. This chromic acid reagent was then added dropwise, with stirring, to the solution of 2-hexen-4-ol, keeping the temperature at or near —15°C.

The crude ethyl propenyl ketone so formed was repeatedly extracted with small portions of diethyl ether and the ether solution was washed successively with aqueous sodium bicarbonate solution (3%) and water and was dried over anhydrous sodium sulphate.

Distillation of the solvent gave a residue (12 gm.) of ethyl propenyl ketone which was purified by gas-chromatographic separation, using firstly a column of diglycerol supported on "Celite" at 100°C with hydrogen as the carrier gas, and secondly a column of diethylene glycol succinate supported on siliconised "Celite" at 120°C, also using hydrogen as the carrier gas.
Cigarettes were prepared as in Example I, using 50 micrograms of ethyl propenyl ketone per gram of tobacco for the treated cigarettes. On smoking, the treated cigarettes were strongly preferred to the control cigarettes and tests using higher concentrations of the ketone showed that it was acceptable up to concentrations of 2,000 micrograms per gram of tobacco.

EXAMPLE III.—DI-(4-KETO-2-PENTYL) ADIPATE

Dry redistilled 4-hydroxypentan-2-one (21.7 gm.) and anhydrous pyridine (16.7 gm.) were dissolved in anhydrous diethyl ether (150 ml.) and cooled to —20°C. Redistilled adipic chloride (19.5 gm.) dissolved in anhydrous diethyl ether (150 ml.) was added slowly to the cooled mixture, keeping the temperature below —15°C. On completion of the addition, the precipitate formed (39.1 gm.) was filtered, washed with diethyl ether and rejected. The filtrate and washings were combined and treated in a rotary evaporator at 40°C and a reduced pressure of 0.1 torr to remove the solvent and volatile impurities. The residue, crude di-(4-keto-2-pentyl) adipate (2.1 gm.) was purified by chromatography on a silica gel (“Bio-rad”—325 mesh per inch) using a mixture of equal volumes of 60-80°C petroleum ether and diethyl ether as eluant.

Cigarettes were prepared as in Example I, using 1,000 micrograms of the ester per gram of tobacco. The ester was sprayed on the cut tobacco in the form of a solution in diethyl ether or acetone, suitably in concentration of about 0.5% by weight. On smoking, the treated cigarettes were strongly preferred to the control cigarettes.

EXAMPLE IV.—4-KETO-2-PENTYL BENZOATE

Dry redistilled 4-hydroxypentan-2-one (16.6 gm.) and anhydrous pyridine (12.9 gm.) were dissolved in anhydrous diethyl ether (150 ml.) and a solution of redistilled benzoyl chloride (22.9 gm.) in anhydrous diethyl ether (150 ml.) was added at 25°C. After standing of the solution overnight, the precipitate formed was filtered off, washed with diethyl ether and rejected.

The filtrate was washed with 5% aqueous sodium hydroxide solution, then with 1% aqueous sulphuric acid solution and finally with water. After drying over anhydrous sodium sulphate, the volatile material and solvent were removed, using a rotary evaporator at 100°C and 0.1 torr. The residue, 4-keto-2-pentyl benzoate (11.0 gm.), was found to be substantially pure by infra-red analysis.

Cigarettes were prepared as in Example IV, using 50 micrograms of the ester per gram of tobacco. On smoking, the treated cigarettes were found not to be preferred by the smoking panel and to be inferior in taste to control cigarettes.

The propenyl ketones, especially the methyl and ethyl ketones, have light etheral aromas which, when the ketones are added to tobacco, are not noticeable in themselves, but blend with and enhance the flavour of the tobacco smoke, producing a markedly smoother smoke. Iso-propenyl and tert-butyl propenyl ketones are similarly effective, while the cyclohexyl propenyl ketone also adds a slight characteristic flavour of its own, reminiscent of figs, which is pleasing to some palates. Propenyl ketones in which the radical R contains more than 6 carbon atoms have more powerful aromas and may be used with tobacco of richer flavour, particularly those which are habitually sauced with flavouring materials such as tobaccos for “American” blends.

The preparation of the ethyl propenyl ketone described in Example II consists of a Grignard-type of reaction followed by an oxidation step following the method of Heilmann, Gaudernas and Arnaud (Bull. Soc. Chim. (1957) 119). Other propenyl ketones, i.e. normal-, iso-, tertiary alkyl and cycloalkyl ketones, can be made in analogous manner.

4. The lower propenyl ketones, i.e. those in which the radical R contains less than six carbon atoms are moderately volatile and may escape from the cigarettes during handling or storage. It is, therefore, advantageous to make the addition to the tobacco in the form of a compound which will remain involatile, preferably until the cigarettes are smoked. Esters with carboxylic acids of alcohols corresponding to the lower ketones are such compounds, which will decompose to give the ketones on heating under the conditions which obtain on the smoking of the tobacco. This is illustrated by the following table:

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Yield of methyl propanoate, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>10</td>
</tr>
<tr>
<td>300</td>
<td>33</td>
</tr>
<tr>
<td>350</td>
<td>56</td>
</tr>
<tr>
<td>400</td>
<td>80</td>
</tr>
</tbody>
</table>

Di-(4-keto-2-pentyl) adipate

Temperature, °C.

<table>
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<td>350</td>
<td>56</td>
</tr>
<tr>
<td>400</td>
<td>80</td>
</tr>
</tbody>
</table>

4-keto-2-pentyl benzoate

Temperature, °C.

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Yield of methyl propanoate, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>18</td>
</tr>
<tr>
<td>300</td>
<td>48</td>
</tr>
<tr>
<td>350</td>
<td>74</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
</tr>
</tbody>
</table>

For the present purpose, it is essential that the ester should not volatilise appreciably, but should decompose appreciably, at a temperature of about 300°C, the temperature just behind the burning coal of a cigarette. While both the esters of Examples III and IV decompose appreciably as shown by the table, the benzoate ester of Example IV is also appreciably volatile and imparts a distasteful flavour to the cigarette, unlike the adipate ester of Example III, which is less volatile, so that the flavor of the unchanged ester does not reach the smoker's mouth.

Example IV is intended to illustrate the preparation of the ester of a monocarboxylic acid and a keto-alcohol and its decomposition to an unsaturated ketone, rather than the preparation of a desirable flavour-producing involatile additive for tobacco.

Desirable, involatile, esters are the esters of monocarboxylic acids containing 14 or more carbon atoms, of di-carboxylic acids containing 4 or more carbon atoms, and of poly-carboxylic acids, which esters are substantially involatile at temperatures below 400°C, and which decompose to yield at least 15% of the ketone at 300°C. We claim:

1. A process for improving the characteristic flavor of a smoking tobacco which comprises incorporating into the tobacco a minor proportion of at least one substantially involatile flavor improving agent selected from the group consisting of propenyl ketone having the general formula R.CO.CH₂.CH₂.CH₃, in which R is selected from the group consisting of alkyl, tertiary alkyl and cycloalkyl, and a carboxylic ester formed by reacting a carboxylic acid and a beta-keto-alcohol, the carboxylic acid being selected from the group consisting of monocarboxylic acids having at least 14 carbon atoms, dicarboxylic acids having at least 4 carbon atoms and polycarboxylic acids, and a beta-keto-alcohol having the general formula R.CO.CH₂.CH(ΟH).CH₃ in which R is selected from the group consisting of alkyl, tertiary alkyl and cycloalkyl, said ester being substantially involatile at temperatures below about 400°C, and undergoing decomposition of at least about 15% at about 300°C, to yield a propenyl ketone.
2. An improved smoking tobacco which comprises smoking tobacco having incorporated therein a minor proportion of at least one substantially involatile flavor improving agent selected from the group consisting of propenyl ketone having the general formula

\[ R \cdot CO \cdot CH = CH \cdot CH_3 \]

in which \( R \) is selected from the group consisting of alkyl, tertiary alkyl and cycloalkyl, and a carboxylic ester formed by reacting a carboxylic acid and a beta-keto-alcohol, the carboxylic acid being selected from the group consisting of monocarboxylic acids having at least 14 carbon atoms, dicarboxylic acids having at least 4 carbon atoms, and polycarboxylic acids, and a beta-keto-alcohol having the general formula \( R \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CH_3 \), in which \( R \) is selected from the group consisting of alkyl, tertiary alkyl and cycloalkyl, said ester being substantially involatile at temperatures below about 400°C, and undergoing decomposition of at least about 15% at about 300°C to yield a propenyl ketone.

3. An improved smoking tobacco in accordance with claim 2 wherein the flavoring agent is present in amounts of about 0.1 to 2,000 micrograms per gram of tobacco when said agent is a propenyl ketone and in sufficient quantity to yield said amounts of a propenyl ketone when the flavoring agent is a carboxylic ester.

4. An improved smoking tobacco having incorporated therein a minor proportion of a substantially involatile flavor improving agent which comprises propenyl ketone having the general formula \( R \cdot CO \cdot CH = CH \cdot CH_3 \), in which \( R \) is selected from the group consisting of alkyl, tertiary alkyl and cycloalkyl, wherein the propenyl ketone is released into the smoke stream under the influence of heat from the burning tobacco so as to modify and improve the characteristic flavor of the tobacco.

5. An improved smoking tobacco in accordance with claim 4 in which the flavor improving agent is a propenyl ketone.

6. An improved smoking tobacco in accordance with claim 4, in which the flavor improving agent is methyl propenyl ketone.

7. An improved smoking tobacco in accordance with claim 4 in which the flavor improving agent is ethyl propenyl ketone.

8. An improved smoking tobacco in accordance with claim 4 in which the flavor improving agent is isopropyl propenyl ketone.

9. An improved smoking tobacco in accordance with claim 4 in which the flavor improving agent is tert-butyl propenyl ketone.

10. An improved smoking tobacco in accordance with claim 4 in which the flavor improving agent is cyclohexyl propenyl ketone.

11. An improved smoking tobacco having incorporated therein a minor proportion of a substantially involatile flavor improving agent which comprises a carboxylic ester formed by reacting a carboxylic acid and a beta-keto-alcohol, the carboxylic acid being selected from the group consisting of monocarboxylic acids having at least 14 carbon atoms, dicarboxylic acids having at least 4 carbon atoms, and polycarboxylic acids, and a beta-keto-alcohol having the general formula

\[ R \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CH_3 \]

in which \( R \) is selected from the group consisting of alkyl, tertiary alkyl and cycloalkyl, said ester being substantially involatile at temperatures below about 400°C, and undergoing decomposition of at least about 15% at about 300°C to yield a propenyl ketone.

12. An improved smoking tobacco in accordance with claim 11 in which the flavor improving agent is di-(4-keto-2-phenyl) adipate.

References Cited

UNITED STATES PATENTS

3,268,589 8/1966 Rowland 131—144X

MELVIN D. REIN, Primary Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,403,686
October 1, 1968

Keith Douglas Kilburn et al.

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

Column 3, line 45, "sulphase" should read -- sulphate --. Column 5, line 3, "proposition" should read -- proportion --; line 28, "incorporarted" should read -- incorporated --. Column 6, line 34, "phenyl" should read -- penty1 --.

Signed and sealed this 3rd day of March 1970.

(SEAL)
Attest:
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Commissioner of Patents