ABSTRACT

This disclosure is directed to a tobacco flavor enhancer from the reaction of valine with a sugar, other hydroxycarbonyl compound, or dicarbonyl compound. The reagents are heated in the presence of a solvent, optionally including a catalyst in the form of a flavanoid or hydroxyacid. The reaction mixture can be used directly in tobacco compositions, or can be stripped, and either or both the volatile and nonvolatile portion can be used in tobacco compositions.

14 Claims, No Drawings
BACKGROUND OF THE INVENTION

Numerous workers have investigated the reaction between amino acids and carbonyl compounds or sugars. This reaction is known as nonenzymatic browning and has been studied largely because of the ultimate production of brown pigments in foods. An intermediate or side reaction results in the production of volatile materials and certain less volatile residues which have not been as extensively studied. However, it has been appreciated that these materials produce interesting flavors and aromas.

The production, from amino acids and carbonyl compounds or sugars, of substances with desirable flavors and aromas, and the methods of using these substances, have raised several problems. For example, the flavors and aromas produced may not be desirable, or desirable products may be masked by the presence of other products. In addition, desirable products may be destroyed if maintained at elevated temperatures or upon reaction with other components. Furthermore, important differences may exist in the suitability of the final product depending on the particular amino acid used in the procedure.

Japanese Patent No. 9,239/71 discloses the preparation of specific condensates of sugars with amino acids, which are added to tobacco products. As the tobacco is smoked the condensates are thermally decomposed and a fragrance is released.

It is an object of this invention to provide an improved method for the reaction of amino acids and sugars or other carbonyl compounds. A further object is the production of useful substances from the reaction of an amino acid, preferably valine, and a sugar or carbonyl compound, to provide tobacco compositions incorporating such substances. These and other objects are set forth in great detail in the accompanying detailed specification.

SUMMARY OF THE INVENTION

This invention is directed to a tobacco composition employing mixtures which are desirable as flavorants and flavor enhancers for tobacco products. More specifically it relates to the reaction of an amino acid with a sugar or carbonyl compound at an elevated temperature in the presence of a solvent. The reaction may be carried out with or without the inclusion of a substance acting as a catalyst, which has the effect of enhancing the aroma and flavor of the tobacco to which the mixture is applied.

The amino acid employed in the process of this invention is primarily valine, but mixtures of amino acids such as those derived by hydrolysis of proteins with a high valine content may also be used. Either optical isomer of valine is suitable in this invention.

The reagent with which the amino acid is reacted in the process of this invention may be a sugar or other carbonyl compound. Preferred sugars are pentoses such as xylose, and hexoses such as glucose or fructose. Disaccharides such as maltose, or higher polysaccharides such as raffinose may be used, but reducing sugars are preferred due to the shorter times and lower temperatures necessary for running the reactions. Other carbonyl compounds which may be used in place of sugars are, for example, hydroxyketones, such as dihydroxyacetone, or dicarbonyl compounds such as pyruvaldehyde.

The catalyst used in the method of the invention may be a flavanoid, such as quercetin or rutin, or a hydroxycacid, such as ascorbic acid.

The solvent used for carrying out the reactions specified according to this invention may be any convenient liquid, such as polyhydroxylic solvents, mineral or vegetable oils, or water. However, polyhydroxylic solvents such as glycerol or propylene glycol are preferred, since their boiling points are in the temperature range useful in the method of the invention, and they are compatible with existing methods of tobacco processing.

In the method of this invention the amino acid and carbonyl compound are added to the solvent, the catalyst added, and the mixture heated to 100°C to 200°C (preferably 120°C to 200°C) for 0.5 to 5 hours, depending on the combination of materials used. A condenser may be employed, but it is not always necessary. The reaction is usually complete when bubbling ceases. The molar ratio of amino acid to carbonyl compound can be from about 1:0.5–10, with a ratio of 1:4–5 being optimum in most cases. The weight ratio of amino acid to the solvent used may be about 1:1 to 200, but ratios of 1:10 to 100 are preferred. Weight ratios of catalyst to amino acid may be 0–100 percent, but levels of 0.5–10 percent are preferred.

The preferred reaction temperature for reducing sugars, hydroxycarbonyl compounds or dicarbonyl compounds is 150°C to 160°C. This range of temperatures usually results in reaction times of 45 to 60 minutes. Higher temperatures tend to produce objectionable, burnt aromas, and lower temperatures produce inconveniently long reaction times. In the case of nonreducing sugars, such as sucrose or raffinose, reaction rates are much lower, and higher temperatures, longer reaction times, or a combination of these must be employed.

The reaction mixtures prepared according to this invention are useful in improving the fragrance of tobacco and tobacco products, and in reducing throat irritation.

The nonvolatile portion of the reaction mixture is useful especially in poorer tobaccos or those which have been aged for shorter than normal periods of time. The usefulness of this material derives principally from its ability to reduce or mask the "green-grassy" taste associated with these tobaccos. Another property of the nonvolatile part of the reaction mixtures is the enhancement of desirable flavor notes of the particular tobacco to which it is applied, while suppressing undesirable harsh, or irritating properties.

In most of the reaction mixtures prepared according to this invention, the stripping operation is not absolutely necessary, especially if some of the more volatile materials are allowed to escape during the reaction. Nearly all of the desirable properties produced during smoking tobacco products containing these mixtures are attributable to the nonvolatile portion.

In addition to stripping, the reaction mixture may be improved by extraction with an immiscible solvent,
such as ether, methyl isobutyl ketone, or isobutyl acetate. This extraction is usually done after the mixture has been diluted somewhat with water, and may be carried out as either a batch or continuous process.

Much the same effect as extraction can be accomplished by subjecting the total reaction mixture to dialysis, using regenerated cellulose, or other suitable membrane. This process removes all the low molecular weight materials, resulting in an aeous solution of browning pigments, which may be isolated by evaporating the water. These pigments possess all of the desirable properties of the total reaction mixture when applied to tobacco at appropriate levels. Thus, according to the method of this invention, it is possible to preferentially remove the undesirable intermediates, and add only those materials which are desirable for tobacco products.

The above properties of the reaction mixtures are also applicable in the case of reconstituted tobacco products. Undesirable taste properties of these tobaccos are often encountered, which are related to the green taste of poor tobaccos, or the papery taste of stem material. The additive has the effect of masking these undesirable tastes, reducing throat irritation and sting, and enhancing natural tobacco taste.

In practice, the unstripped reaction mixture can be applied to tobacco in an amount equivalent to about 0.001 to 2.0 percent, based on the amount of amino acid used at the beginning of the reaction and the amount of solvent employed. The exact percentage depends on the effect desired. The material which has been stripped of volatiles is also applied at these levels, but usually somewhat higher than the unstripped material. The volatile portion which collects in the traps during the stripping operation is useful at about 0.001 to 0.05 percent, based on its total solids content, which is determined while in ether solution.

The methods of applying these materials are known to those practiced in the art, but basically consist of spraying or dipping, preferably the former. One very convenient method is the incorporation of the material into the casing formulation and applying during the customary casing operation. Another method is to mix the material with ethanol or other suitable solvent and to incorporate into the top-dressing, which is then applied in the normal manner.

The following specific examples serve to illustrate the procedure used in preparing the flavorants and flavor enhancers described in this disclosure.

**EXAMPLE I**

A mixture of 1 g DL-valine, 7.2 g D-glucose, 100 mg rutin and 100 ml glycerol was heated to 160° for 45 min. An odor of chocolate with burnt sugar and peanut undertones was noticed on cooling.

**EXAMPLE II**

A mixture of 20 g L-valine, 2 g rutin, and 24 g D-glucose was added to 200 ml glycerol and heated to 160° for 1 hour, using a reflux condenser to prevent loss of volatiles. When cooling, the mixture was passed slowly through a stripper which consisted of a steam-heated glass coil connected in series to a receiving flask, two liquid air-cooled traps, and a vacuum pump. The volatile materials stripped off in the coil were trapped, and then washed out of the traps with ether.

After separating and reextracting the water present in the traps, the combined ether solutions were dried over sodium sulfate, and a total solids determination showed that the volatiles weighed 470 mg.

The nonvolatile portion of the reaction, which included the glycol solvent, had a slight odor of chocolate, and weighed 253 g.

The following additional samples (Table I) serve to illustrate the variations of the invention that produce useful flavorants and flavor enhancers.

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Wt. of Valine (g)</th>
<th>Wt. (g)</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Vol. (ml)</th>
<th>Reaction Conditions</th>
<th>Aroma Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>1.0 D-Glucose</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
<td>Glycerol</td>
<td>7</td>
<td>160°/45 min</td>
</tr>
<tr>
<td>IV</td>
<td>1.0 D-Glucose</td>
<td>1.5</td>
<td>Rutin</td>
<td>1.0</td>
<td>Glycerol</td>
<td>7</td>
<td>160°/45 min</td>
</tr>
<tr>
<td>V</td>
<td>1.0 D-Maltose</td>
<td>2.4</td>
<td>—</td>
<td>—</td>
<td>Glycerol</td>
<td>10</td>
<td>160°/45 min</td>
</tr>
<tr>
<td>VI</td>
<td>1.0 D-Raffinose</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>Glycerol</td>
<td>10</td>
<td>155°/70 min</td>
</tr>
<tr>
<td>VII</td>
<td>1.0 D-Sucrose</td>
<td>1.5</td>
<td>Rutin</td>
<td>0.1</td>
<td>Glycerol</td>
<td>10</td>
<td>155°/70 min</td>
</tr>
<tr>
<td>VIII</td>
<td>1.0 D-Fructose</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
<td>Glycerol</td>
<td>100</td>
<td>160°/45 min</td>
</tr>
<tr>
<td>IX</td>
<td>1.0 Dihydroxyacetone</td>
<td>1.54</td>
<td>—</td>
<td>—</td>
<td>Glycerol</td>
<td>10</td>
<td>150°/60 min</td>
</tr>
<tr>
<td>X</td>
<td>1.0 Pyruvaldehyde*</td>
<td>4.1</td>
<td>—</td>
<td>—</td>
<td>Glycerol</td>
<td>10</td>
<td>150°/60 min</td>
</tr>
<tr>
<td>XI</td>
<td>10.0 D-Glucose</td>
<td>15.0</td>
<td>Rutin</td>
<td>0.1</td>
<td>Glycol 4-propylene glycol</td>
<td>100</td>
<td>150°/60 min</td>
</tr>
<tr>
<td>XII</td>
<td>10.0 D-Glucose</td>
<td>15.0</td>
<td>Rutin</td>
<td>0.1</td>
<td>D-Sorbitol</td>
<td>120g</td>
<td>160°/45 min</td>
</tr>
<tr>
<td>XIII</td>
<td>10.0 D-Glucose</td>
<td>15.0</td>
<td>Quercetin</td>
<td>0.1</td>
<td>Glycol</td>
<td>100</td>
<td>160°/45 min</td>
</tr>
<tr>
<td>XIV</td>
<td>10.0 D-Glucose</td>
<td>15.0</td>
<td>Ascorbic Acid</td>
<td>0.1</td>
<td>Glycol</td>
<td>100</td>
<td>160°/45 min</td>
</tr>
</tbody>
</table>

*3% aqueous solution.

A preferred method of preparation is illustrated in Example XV.

**EXAMPLE XV**

A mixture of 20 g DL-valine, 157 g D-glucose, 0.20 g rutin and 600 g glycerol was heated to 160° in an open reaction vessel, and maintained at this temperature for 1 hour, with continuous stirring. The mixture, on cooling, was diluted with 500 ml water and extracted with three 200 ml portions of ether. The aqueous-glycerol solution was heated on a steam bath for 2 hours to remove remaining traces of ether. The resulting solution had a specific gravity of 1.213. Dialysis of an aliquot against distilled water, using regenerated cellulose tubing as the semipermeable membrane, showed that 18.6 g of browning pigments were contained in the total so-
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Specific examples of incorporating the reaction products from the above examples into tobacco products are as follows:

EXAMPLE XVI

A solution of 0.1 g of the mixture prepared as set forth in Example I, in 2 ml 50% aqueous alcohol, was sprayed onto 100 g of a cased and cut commercial blend of tobaccos, including some reconstituted tobacco. Cigarettes were prepared from this tobacco and evaluated by an experienced panel of smokers. When the cigarettes were compared with untreated control cigarettes, the presence of the additive produced a rather remarkable effect on irritation and impact, producing a smoke which was quite smooth. The flavor spectrum was affected by the introduction of a heavy-sweet, cocoa-like fragrance.

EXAMPLE XVII

The volatile portion from Example II was diluted to 50 ml with 95% ethanol. A 0.1 ml aliquot of this solution was diluted to 10 ml with 50% aqueous alcohol and sprayed onto 100 g of low grade Virginia tobacco. Cigarettes made from this tobacco had an accented "Virginia" tobacco taste.

EXAMPLE XVIII

A solution of 0.05 g of the nonvolatile (stripped) portion from Example II, in 1 ml of 50% aqueous alcohol, was sprayed onto 100 g of low grade Virginia tobacco. Cigarettes made from this tobacco exhibited a reduction of the "green-grassy" taste noticed in the control cigarettes. The mixture also produced a rounding of the flavor and a much smoother smoke.

EXAMPLE XIX

The procedure of Example XVIII was repeated using a low grade Burley tobacco. The cigarettes made from this tobacco displayed a reduction in impact and sharpness when compared to a control, and the desirable burley fragrance was enhanced.

EXAMPLE XX

The procedure of Example XVIII was repeated using reconstituted tobacco. The cigarettes prepared from this tobacco, when compared to control cigarettes, had a reduced "oak-leaf" taste, and a sweet, spice-like flavor.

EXAMPLE XXI

The procedure of Example XX was repeated, except that a solution of 0.1 g of the nonvolatile portion in 1 ml 50% aqueous alcohol was used. Cigarettes prepared from this tobacco exhibited enhanced tobacco taste, along with reduced throat irritation and mouth pepperiness.

EXAMPLE XXII

A solution of 0.1 g of the mixture prepared as set forth in Example XI, in 2 ml 50% aqueous alcohol, was sprayed onto 100 g of a cased and cut commercial blend of tobaccos and evaluated as in Example XVI. The smoke from cigarettes thus prepared showed a noticeable reduction in impact and amplitude, and a slight reduction in the oak-leaf taste associated with reconstituted tobacco. The flavor showed less pepperiness and was somewhat sour.

EXAMPLE XXIII

A solution of 0.1 g of the mixture prepared as set forth in Example XIV, in 2 ml 50% aqueous alcohol, was sprayed onto 100 g of a commercial blend of tobaccos and evaluated as in Example XVI. The cigarettes produced a slightly lower impact and amplitude of flavor than the untreated control, with an increase in sour-green notes.

EXAMPLE XXIV

A solution of 12 mg of the pigments isolated as described in Example XV, in 2 ml of a 50% aqueous alcohol solution, was sprayed onto 100 g of unflavored cut tobacco, and cigarettes prepared accordingly. The smoke produced by these cigarettes was described by the flavor panel as having a lesser degree of harshness and irritation than a similarly prepared control, with better balance, and more sweet taste and tobacco fragrance.

This invention has been described in terms of specific embodiments set forth in detail. Alternative embodiments will be apparent to those skilled in the art in view of this disclosure, and accordingly such modifications are to be contemplated within the spirit of the invention as disclosed and claimed herein.

We claim:

1. A tobacco composition comprising tobacco and a minor amount of a flavor enhancer wherein the enhancer is a non-volatile solution of browning pigments made by heating between about 120° - 200°C a reaction mixture containing a solvent, valine and a carbonyl compound selected from the group consisting of a sugar, dihydroxy acetone and pyruvaldehyde.

2. The composition of claim 1 wherein the solvent is selected from the group consisting of glycerol and propylene glycol.

3. The composition of claim 1 wherein the reaction mixture contains a catalyst.

4. The composition of claim 3 wherein the catalyst is selected from the group consisting of rutin, quercetin, and ascorbic acid.

5. A tobacco composition comprising tobacco and a minor amount of a flavor enhancer; said enhancer comprising the browning pigments separated from the reaction product of a mixture heated to between about 120°C and 200°C of a solvent, valine and a carbonyl compound selected from the group consisting of sugar, dihydroxy acetone and pyruvaldehyde.

6. The composition of claim 5 wherein the solvent is selected from the group consisting of glycerol and propylene glycol.

7. The composition of claim 5 which further comprises a catalyst.

8. The catalyst of claim 6 selected from the group consisting of rutin, quercetin and ascorbic acid.

9. The composition of claim 1 wherein the sugar is a pentose or hexose.

10. The composition of claim 5 wherein the sugar is a pentose or hexose.

11. The composition of claim 1 wherein the sugar is a reducing sugar.

12. The composition of claim 11 wherein the temperature is between about 150°C and 160°C.

13. The composition of claim 5 wherein the sugar is a reducing sugar.

14. The composition of claim 13 wherein the temperature is between about 150°C and 160°C.